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EFFECT OF ACTIVATION BY OXIDIZING GAS AND ALKALINE SOLUTION ON PROPERTIES OF ACTIVATED CARBON FROM PARA WOOD

Miss Phawika Chuenklang

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By Miss Phawika Chuenklang
Department Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Tharapong Vitidsant, Ph.D.

Accepted by Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

Deputy Dean for Administrative Affairs
……………………………………………. Acting Dean of Faculty of Science
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(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

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(Suchaya Nitivattananon, Ph.D.)

ภวิกา ชื่นคลัง : ผลของการกระตุ้นโดยแก๊สออกซิไดซ์และสารละลายด่างต่อสมบัติของถ่านกัมมันต์จากไม้ยางพารา (EFFECT OF ACTIVATION BY OXIDIZING GAS AND ALKALINE SOLUTION ON PROPERTIES OF ACTIVATED CARBON FROM PARA WOOD)
อ. ที่ปรึกษา รศ.ดร ธราพงษ์ วิทิตศานต์ : 111 หน้า, ISBN 974 – 03 – 1339 - 6

งานวิจัยนี้ทำการศึกษาผลของการกระตุ้นโดยแก๊สออกซิไดซ์ และสารละลายด่าง ต่อสมบัติของถ่านกัมมันต์จากไม้ยางพารา โดยในการทดลองนี้ยังประกอบไปด้วยการคาร์บอไนซ์ และการกระตุ้น ตัวแปรที่ศึกษาคือ อุณหภูมิ (350-450 องศาเซลเซียส) และเวลาที่ใช้ในการคาร์บอไนซ์ (45, 60, 90 และ 120 นาที) อุณหภูมิ และเวลาที่เหมาะสมในการคาร์บอไนซ์ คือ ที่อุณหภูมิ 400 องศาเซลเซียส เป็นเวลา 45 นาที ซึ่งจะได้ร้อยละผลิตภัณฑ์ 27.51 มีปริมาณคาร์บอนคงตัวร้อยละ 70.46 สารระเหยร้อยละ 25.89 และเถ้าร้อยละ 2.31 จากนั้นถ่านไม้ยางพาราจำถูกกระตุ้นโดยใช้ แก๊สออกซิไดซ์ สารละลายด่างของ โปตัสเซียมไฮดรอกไซด์ และ โซเดียมไฮดรอกไซด์ ตัวแปรที่ใช้ศึกษาคือ อุณหภูมิ, เวลา, ขนาดของถ่านไม้ยางพารา รวมถึง อัตราส่วนของถ่านไม้ยางพารา ต่อ ปริมาณด่างที่ใช้ในการกระตุ้น จากการทดลองพบว่า ภาวะที่เหมาะสมที่ใช้ในการกระตุ้นทางกายภาพคือ กระตุ้นที่อุณหภูมิ 800°C เป็นเวลา 3 ชั่วโมง โดยใช้ถ่านจากไม้ยางพาราขนาด 0.60-1.18 มิลลิเมตร ถ่านกัมมันต์ที่ได้มีร้อยละผลิตภัณฑ์ 44.44 ความหนาแน่นเชิงปริมาตร 0.21 กรัม/ลูกบาศก์เซนติเมตร ค่าเถ้าร้อยละ 7.33 ค่าการดูดซับไอโอดีน 512 มิลลิกรัม/กรัม และค่าการดูดซับเมทิลีนบลู 154 มิลลิกรัม/กรัม ส่วนภาวะที่เหมาะสมในการกระตุ้นทางเคมี ทั้งที่ใช้ โปตัสเซียมไฮดรอกไซด์ และ โซเดียมไฮดรอกไซด์ เป็นสารกระตุ้นคือ กระตุ้นที่อุณหภูมิ 700 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง ใช้ถ่านจากไม้ยางพาราขนาด 0.60-1.18 มิลลิเมตร ถ่านกัมมันต์ที่ได้จากการกระตุ้นโดยใช้ โปตัสเซียมไฮดรอกไซด์ เป็นสารกระตุ้น มีคุณภาพดีกว่าถ่านกัมมันต์ที่ได้จากการกระตุ้นโดยใช้ โซเดียมไฮดรอกไซด์ เนื่องมาจาก โซเดียมไฮดรอกไซด์เกิดปฏิกิริยากับถ่านอย่างรุนแรงทำให้เกิดรูพรุนที่มีขนาดใหญ่ ถ่านกัมมันต์ที่เตรียมได้จากโปตัสเซียมไฮดรอกไซด์ มีค่าร้อยละผลิตภัณฑ์ 48.00 ความหนาแน่นเชิงปริมาตร 0.1138 กรัม/ลูกบาศก์เซนติเมตร ค่าเถ้าร้อยละ 5.24 % ค่าการดูดซับไอโอดีน 1069 มิลลิกรัม/กรัม ค่าการดูดซับเมทิลีนบลู 202 มิลลิกรัม/กรัม และค่าพื้นที่ผิวรูพรุน 943.35 ตารางเมตร/กรัม ซึ่งเมื่อทำการกระตุ้นโดยใช้ โซเดียมไฮดรอกไซด์ จะให้สมบัติที่ต่ำกว่า

ภาควิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต……………………………………
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่ออาจารย์ที่ปรึกษา……………………………..
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This research was the study of the effect of activation by oxidizing gas and alkaline solution on properties of activated carbon from Para wood. The experiment was included both carbonization and activation. The variable studied was temperature (350 – 450°C) and carbonized time (45, 60, 90, and 120 minutes) in carbonization step. The suitable carbonization condition was at temperature 400 °C for 45 minutes with 27.51 % yield, 70.46 % fixed carbon, 25.89 % volatile matter and 2.31 % ash. Para wood char was activated by oxidizing gas and by alkaline solution such as KOH and NaOH. Studied variables were activation temperature, activation time and size of Para wood char including ratio of char per alkaline. The experimental results were found that the suitable condition for physical activation was 800 °C in 3 hours using char from Para wood sized of 0.60-1.18 mm. Activated carbon obtained were 44.44% yield, 0.21 g/cm^3 bulk density, 7.33% ash, iodine number 512 mg/g and methylene blue number 154 mg/g. Whereas the suitable condition for chemical activation both using KOH and NaOH as activating agent was 700 °C for 3 hours using char from Para wood size 0.60 – 1.18 m. Activated carbon prepared from KOH gave higher quality than NaOH because stronger alkaline, NaOH developed larger pores size. The activated carbon obtained by using KOH was 48% yield, 0.1138 g/cm^3 bulk density, 5.236% ash, iodine number 1069 mg/g, methylene blue number 202 mg/g and BET surface are 943.35 m^2/g whereas using NaOH gave lower properties.

Program Petrochemistry and Polymer science Student's signature……………………………

Field of study Petrochemistry and Polymer science Advisor's signature………………………

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ABBREVIATIONS

T : Temperature (^{o}C)

t : Time (hr)

% Y : % Yield

% M : % Moisture

% VM : % Volatile matter

% FC : % Fixed carbon

BD : Bulk density (g/cm^{3})

IA : Iodine number(mg/g)

MB : Methylene blue number (mg/g)

$S_{\text{B.E.T.}}$: B.E.T. surface area (m^{2}/g)

S_{micro} : Micropore area (m^{2}/g)

S_{external} : External surface area (m^{2}/g)

V_{total} : Total pore volume (cm^{3}/g)

V_{micro} : Micropore volume (cm^{3}/g)

$V_{\text{non-micro}}$: Non-micropore volume(cm^{3}/g)

CHAPTER I

INTRODUCTION

1.1 Para wood

The value of the rubber tree till recently has been mainly for its latex. But this is slowly changing. The utilization of the rubber tree in a holistic sense is now being give focus: for instance, the tree is being looked at from the environment angle: plant nutrients and other useful chemicals are being soured from effluents and waste from rubber processing and above all rubber timber is now a valuable resources. Over the last decade the demand for rubber timber had been increasing rapidly. The term “Para wood” is usually given to the timber of the species *Hevea brasiliensis*. (1)

Figure 1.1 Para wood

The good working qualities of rubber timber, its durability, pleasant appearance and beautiful grains make it suitable for numerous end uses. Wood for making furniture to padded or upholstered furniture. Para wood in solid or laminated form is used in manufacturing of moldings, parquet, household utility items, toys and many other finished items. It is also used for making plywood, particle board, layered construction materials, fibre board, wood cement board, composite woods, paper, charcoal, etc. Moreover, Para wood is still an important source of fuel in many areas.

The total growing area of natural rubber (NR) in Asia natural rubber producing countries (ANRPC) in 1994 was about 7.87 million hectares. **Table 1.1** shows the planted area in 1994 in the member countries. The estimated area replanted in 1994 is given in **Table 1.2.**

Table 1.1 Growing area of natural rubber in ANRPC countries 1994 (X100 hectares). (1)

Country	Area
India	516
Indonesia	3,448
Malaysia	1,760
Sri Lanka	192
Thailand	1,940

Table 1.2 Area replanted in 1994 (X1000 hectares). (1)

Country	Area
India	7.5
Indonesia	39.2
Malaysia	30.0
Sri Lanka	1.6
Thailand	37.0

Assuming the yield of wood from rubber trees at 180 cubic meters per hectares. The potential out put of Para wood from these countries in 1994 would add up to 20.75 million cubic meters. Again, based on the usual assumption that 180 cubic meter of Para wood would result in 45 cubic meters. (1)

Wood consumption in Thailand was about 4 million cubic meters in 1992 of which only about 110,000 cubic meters was produced domestically. The balance was imported. Thailand exported furniture parts valued at 16,738 million Bahts ($ 661.8 million) in 1993 and the figure for 1994 was 19,530 million Bahts ($ 779.6 million), representing an increase of less than 17 %. A sizable portion of the furniture parts was made from Para wood. Para wood could be expected to meet a major part of the future need in Thailand. (1)

1.2 Activated carbon (6,7)

Activated carbon has been in use for thousands of year. The major development of activated carbon began during World War I, when hard granular activated carbon (GAC) was manufactured for use in gas masks. In the last 50 years the technology involved in activated carbon manufacture has advanced. Powdered activated carbon (PAC) is extensively used in water purification processes together with granulated activated carbon. PAC is associated with larger pore diameters than GAC.

Activated carbon can be defined as highly porous, carbonaceous materials. They very large porosity provides a large surface area, which results in exceptional adsorptive properties. Basically, the porosity is only a means, to provide the adsorptive properties that make activated carbon of practical use. In the industry, carbons are therefore characterized by adsorptive properties rather than pore structures.

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

1.3 Objectives

This work shows the studies of optimum condition, which effects the activation by oxidizing gas and alkaline solutions on properties of activated carbon from Para wood. The objectives of this work are following:

1. To find effective parameters and optimum conditions for the production of activated carbon from Para wood.
2. To study physical and chemical properties of the produced activated carbon.

1.4 Scope of the research

Production of activated carbon from Para wood by oxidizing gas and alkaline solution activation, the appropriate parameters such as temperatures, time, ratio of steam and CO_2 , size of raw material and concentration of alkaline solution were studied. The following list outlines the procedures:

1. Literature survey and in-depth study of this research work.
2. Carbonization of Para wood crushed and sieved to three different particle sizes of 0.60 – 1.18, 1.18 - 2.36 and 2.36 - 4.75 mm.
3. Proximate analysis of Para wood.
4. Production of activated carbon from Para wood by oxidizing gas activation and manipulating the following parameters so as to attain the optimum condition:
    (a) The effect of activation temperature.
    (b) The effect of activation time.
    (c) The effect of size of Para wood.

5. Production of activated carbon from Para wood by alkaline solution activation and manipulating the following parameters so as to attain the optimum condition:
    (a) The effect of concentration of alkaline solution.
    (b) The effect of activation temperature.
    (c) The effect of activation time.
    (d) The effect of particle size of Para wood.
    (e) The effect of reagent for activation
6. Investigation of the properties of the activated carbon such as % yield, % ash, bulk density, iodine number, methylene blue number, S.E.M. and B.E.T. surface area.
7. Summarizing the results.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Formation and structure of wood

2.1.1 Wood source (1)

Wood is obtained from two broad categories of plants known commercially as softwoods and hardwoods. These names cannot be used universally to refer to the actual physical hardness of all woods because some soft wood are quite hard and some hard wood are soft.

From a more scientific perspective, softwoods are tree species of a class of plant called gymnosperms (seeds are borne naked and hardwoods are woody, dicotyledonous (two seed leaves) angiosperms (seeds are brone in a fruit structures).

The softwoods are also referred to conifers because they produce seed cones, pollen cones, or both. The conifers have needlelike or saclike leaves and appear to be evergreen in that they retain new leaves for several years.

Hardwood have leaves that are generally board or bladelike, and many commercial species in temperate climates- are deciduous, which means they commonly shed their leaves each of the tree's growing season.

2.1.2 Technical nature (1)

Wood is a complex plant tissue composed of several district types of cells. In their fully mature state, the vast majority of wood cells are dead and hollow, and the resulting tissue known technically as secondary xylem is composed essentially of only cell walls and voids. The voids are being the hollow interiors of the cells (or lumens) as shown in **Figure 2.1.** In softwoods, the cell

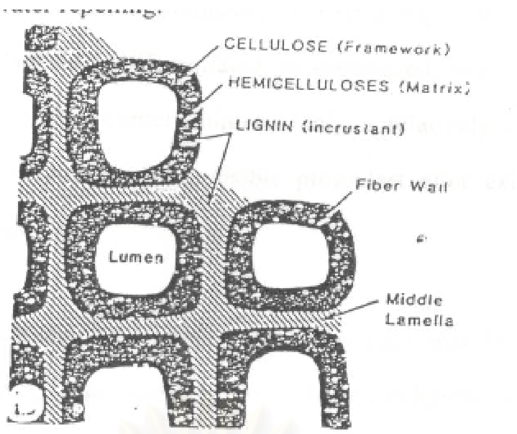

Figure 2.1 Schematic showing the location of major constituents of wood. (1)

making up 90-95 % of wood volume are fibrous in form and are thus termed fibers. Hardwoods, on the other hand, are composed largely of fibers and much wider cells called vessel elements. The vessel elements are joined end-wise to form tubes or vessel along the stem, branch or root axis and are seen as pores on the wood cross section.

From a chemical perspective, wood tissue (including cells and inter cellular substance) is a composites material constructed from a variety of organic polymer. The basic structure or skeletal materials of all wood cell wall is cellulose, hemicelluloses and lignins.

The wood cell wall-cellulose and hemicellulose- have a strong affinity for water molecules in either their liquid or vapor state. Lignin on the other hand, is almost water repelling.

2.1.3 Wood cell production

The sites of wood cell production use the vascular cambium. It is responsible for the manufacture of all initial and subsequent wood tissues. The cambium is a thin, circumferential sheet of cells that produces wood or secondary xylem to the inside (i.e. toward the tree center) and phloem or inner bark tissue to the out side. Xylem functions largely in upward conduction and mechanical support, and phloem act as a conduct for downward movement of photosynthesis (manufactured foodstuffs) and hormones from leaves and buds. Both xylem and phloem also function in a storage capacity, which takes place largely in parenchyma cells (1)

All cells in cambium zone are living cell. However, as xylem derivatives (i.e., developing wood cells) begin a sequence of transformations that will convert them into mature wood elements, they embark on a path of cell specialization or differentiation that lead eventually to cell death.

New xylem derivative may function for a period of time as mother cells, dividing to form other derivatives. Nevertheless, the ultimate fate of most xylem derivatives is self destruction, autolysis, of their living contents, protoplast, and the eventual products are fully differentiated, or specialized, wood cells possessing rather elaborate walls and hollow centers, lumens. Only a relatively small number of cells in wood called parenchynia retain a visible protoplast after exiting the cambial and differentiation zones.

Parenchymas are small, nonfibrous cells that have the special storage on secretary functions. It also composes most (or all in hardwoods) of the wood tissue regions referred to collectively as wood rays. These structures are narrow ribbons of the stem axis **(Figure 2.2)**.

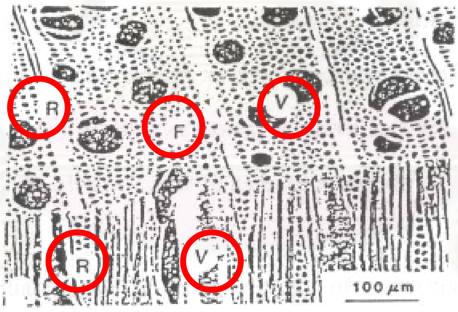

Figure 2.2 SEM of wood rays (R) , vessel or pores (V) and wood fiber (F). (1)

During the division and enlargement phases of wood cell development, the cell wall is thin, deformable, and extensible envelope of material referred to as the primary wall, never the cessation of cell enlargement, however, a secondary wall may begin to be manufactured to the lumen side of the primary wall. Wood fibers, vessel elements, and certain other xylem or phloem elements that function in passive conduction and/or support normally develop a secondary wall **(Figure 2.3)**.

Figure 2.3 Cross-sectional view of fully differentiated wood fibers. The thin cell wall (s) and fiber lumen (L). (1)

2.1.4 Hardwoods

Hard woods contain a substantial volume of fiber cells, but the distinguishing feature of angiosperm xylem is occurrence of vessels are seen on the wood cross section as holes or pores in various patterns **(Figure 2.4)**. Thus, all hardwoods are also referred to as porous wood. (1)

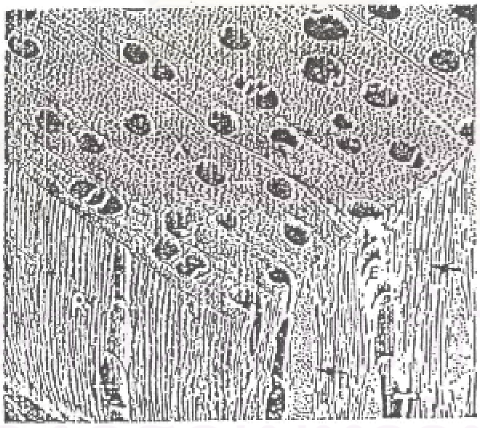

Figure 2.4 Diffuse – porous hard wood, formation of vessels from individual vessel.

An individual vessel or pore consists of a vertical series of short vessel segments, which are joined end to end along the grain. Individual vessels can meander to a limited extent in radial or tangential direction to join, terminate in, or depart from other vessel, but their major function is the vertical translocation of sap. To facilitate this translocation, the ends of all vessel segments are perforate, that is, the ends are open for free flow of liquids between cells. In some hardwoods the vessel segment ends are entirely open (simple), while in others ends contain a series of parallel crossbars (scalariform) or some other design. The particular type of opening here is of considerable value in wood species identification.

Hardwood fiber, because of the presence of vessels, occupy a proportionally smaller volume of wood tissue than softwood fibers do. The fiber themselves are also smaller. The parenchyma cell content of hardwoods is, on the average, much greater than that of softwoods. This situation is a result of the wider rays and greater ray volume of hardwoods and also the relatively high proportion of longitudinal parenchyma.

The volume ratio of vessels to fiber and fiber wall thickness are two important factors influencing the hardness and density of different hardwood species and the permeability of these woods to liquids and gases. Wood grain is also a function of these two parameters.

2.2 Para wood

2.2.1 Technical properties and utilization of Para wood

The most important product of the rubber tree is the latex and all efforts toimprove the rubber tree have been from the point of obtaining higher yield of latex. After exploitation, the rubber tree is felled for replanting with high yielding clones. Till recently, most of the wood from the felled trees was used as fuel. With the depletion of forest in many parts of tropical regions, leading to storage of wood for many industrial and engineering uses, attention has been given to Para wood as an alternative source of timber. Research and development activities on the industrial applications of Para wood are only of recent origin. New developments indicate the possibility of wider use possibility of wider use of Para wood or for a variety of purpose (1)

Rubber trees grow to a height of 25 meters and generally have straight trunks. Usually, at the time of felling, the girth varies between 100 to 110 centimeters, at a height of 125 centimeters of branch wood. At the time of felling, usually it contains 180 to 185 trees per hectare.

2.2.2 Anatomy of Para wood

The texture of the wood is fairly even with moderately straight and slightly interlocking grain. From whitish yellow when freshly cut, the wood turns to light brown as drying progresses. Latex vessel can be found with characteristic smell in some parts of the wood. The wood is soft to moderately hard with an average weight of 515 kilograms per cubic meters at 12 % moisture content. Pores on the cross section are diffused and of medium to large size, mostly solitary but sometimes in short multiples of two three, filled with tyloses. Vessel tissues are conspicuous in radial and tangential faces and are of the order of about 200 micron in diameter. Wood parenchyma are abundantly visible to the naked eye appearing as narrow, irregular and somewhat closely spaced bands forming a net like pattern with rays. The ray of the wood are moderately broad, rather few and fairly wide spread. The pits found between the vessels and rays are half-bordered with narrow width. The length of the fibers is more than 1.0 millimeters on the average and the width is about 22 microns when dry. The cell wall thickness when dry is about 2.8 microns (1).

There is insignificant heart wood formation and no transition appears between sapwood and heartwood, which is confined near the pith. Growth ring or annual rings are not visible in Para wood, unlike many other woods (ring porous woods). However, concentric false sometimes appear on the wood, depending on the presence of tension wood (gelatinous cells) which are fairly common in most of clones. Maximum numbers of such rings are found in the basal portions with decreasing number of towards the top. The tension wood may vary from 15 to 65 % and such erratic distribution tends to give a woolly appearance on the surface of wood. Such distribution and variation are supposed to be responsible for some of the commonly observed defects that may occur during and processing.

2.3 Activated carbon

Activated carbon is a crude form of graphite, the substance used for pencil leads. It differs from graphite by having a random imperfect structure, which is highly porous over a broad range of pore sizes from visible cracks and crevices to molecular dimensions. The graphite structure gives the carbon its very large surface area, which allows the carbon to adsorb a wide range of compounds.

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

2.4 Raw materials for the production of activated carbon (8)

Activated carbon is manufactured from a wide variety of materials but those most frequently used on commercial scale are peat, coal, lignite, wood (sawdust), which should exhibit high adsorption capacity and large volume of the smallest pores (micropores), coconut shells are usually used. The principal properties of manufactured activated carbons depend on the type and properties of raw material used. Any cheap substance with a high carbon and low ash content can be used as raw material for the production of activated carbon.

2.5 Application for activated carbon

Activated carbon is used for gas- and liquid phase adsorption processes. Nearly 80% of about 300,000 ton per year is used for liquid – phase applications and approximately 60,000 ton per year for gas – phase applications; these tables are based on worldwide usage (9). Granulated active carbons are mainly employed for gas adsorption and separations (shown in **Table 2.1**).

Table 2.1 Application for activated carbon.

Vapor phase

Industry	Description	Typical use
Solvent recovery	Recovery of organic solvents to Optimize process economics and Control vapor emissions	Acetate fibres (acetone), pharmaceuticals (methylene chloride), film coating and printing (ethyl acetate), magnetic tape
Carbon dioxide	Purification of carbon dioxide from fermentation processes	Adsorption of alcohol, amines and mercaptans
Industrial Repirators	Adsorption of organic vapors	-
Waste disposal	Disposal of domestic, chemical And clinical waste by high Temperature incineration	Removal of heavy metals and dioxins from flue gas
Cigarettes	Incorporation as either powder or granule in filter tips	Extraction of some harmful elements of cigarette smoke, or taste and flavor control

Table 2.1 Application for activated carbon (continued).

Liquid phase

Industry	Description	Typical use
Potable water treatment	Granular activated carbon (GAC) installed rapid gravity filters	Removal of dissolved organic contaminants, control of taste and odor problems
Soft drinks	Potable water treatment, Sterilization with chlorine	Chlorine removal and adsorption of dissolved organic contaminants
Brewing	potable water treatment	Removal of trihalomethanes(THM) And phenolics
Semi – conductors	Ultra high purity water	Total organic carbon (TOC) reduction
Gold recovery	Operation of carbon in leach (CIL), carbon in pulp (CIP) and heap leach circuits	Recovery of gold from “tailings” dissolved in sodium cyanide
Petrochemical	Recycling of steam condensate For boiler feed water	Removal of oil and hydrocarbon contamination
Groundwater	Industrial contamination of Ground water reserves	Reduction of total organic halogens (TOX) and adsorbable organic halogens (AOX) Including chloroform, tetrachloroethylene And trichloromethane
Industrial waste water	Process effluent treatment to meet environmental legislation	Reduction of total organic halogens (TOX), biological oxygen demand (BOD) and chemical oxygen demand (COD)

2.6 Production of activated carbon

The most desirable method of producing activated carbon is by adjusting processing conduction to control precisely the properties of the end product. This is more cost-effective than changing the precursor to suit changing requirements, but necessitates a consistent material.

Variations occur in precursors in terms of structure and mineral matter content, associated with locality of growth, climate and cropping. Mineral matter is often responsible for preferential gasification during the activation process resulting in meso-and macropore channeling and pitting, and not the preferred microporosity. The carbonization and activation of carbonaceous materials usually produce activated carbon.

2.6.1 Carbonization (or pyrolysis)

This is the most important step in the production process of activated carbon 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 feed 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 apparently as the result of deposition and decomposition of terry substances, these become filled or at least blocked by disorganized ("amorphous") carbon. There are three clear stages in the carbonization process: (a) loss of water in the 27-197 °C range; (b) primary pyrolysis in the 197- 497 °C range with evolution of most gases and tars with formation of the basis structure of the char; (c) concolidation of char structure at 497- 847 °C with a very small weight loss. The resulting carbonization at lower temperatures (400 - 600°C), part of the tar remains in the pores between the crystallites and on there surface. A carbon with a large adsorption capacity, however, can be produced only by activating the corbonized material under such conditions that the activation agent (steam, carbon dioxide, etc.) reacts with the carbon.

2.6.2 Activation

The large internal surface areas of activated carbon are the result of the activation process. Two routes are used to increase porosity: chemical and physical activations. Generally, there are two main types of production of activated carbon:

- By carbonizing material with the addition of activating agents ($ZnCl_2$,$CaCl_2$ H_3PO_4). This method is generally known as “chemical activation”.
- By allowing the inactive carbonized product (prepare by the usual methods of carbonization) to react with usually suitable gaseous substances (steam, carbon dioxide, oxygen). This method is generally known as “physical activation”.

2.6.2.1 Chemical activation

This process involves carbonizing the parent material after impregnation with, e.g., potassium hydroxide, sodium hydroxide, phosphoric acid, zinc chloride, carbonates of alkali metals and metal chlorides. The common feature of these compounds is their ability to act as dehydrating agents which influence the pyrolytic decomposition and inhibit tar information. The temperature range for chemical activation is 400 – 800 ^{o}C. These temperatures are lower than those needed for activation with gaseous agent (physical activation). And important factor in chemical activation is the degree (coefficient) of impregnation; this is the weight ratio of the anhydrous activation salt to dry starting material. The effect of degree of impregnation on the resulting product is apparent from the fact that the volume of salt in the carbonized material equals the volume of pores, which are freed by its extraction. For small degree of impregnation the increase in the total pore volume of the product with increase in the degree of impregnation is due to the in crease in the number of small pores. When the degree of impregnation is father raised the number of larger-diameter pore increases and the volume of the smallest decreases.

During chemical activation the chemistry of pyrolysis changed and the different, macromolecular network system is established with enhanced porosity. The activation agent also changes the chemical nature of the cellulose substance by dehydration, which decomposes the organic substances by the action of heat and prevents the formation of tar.

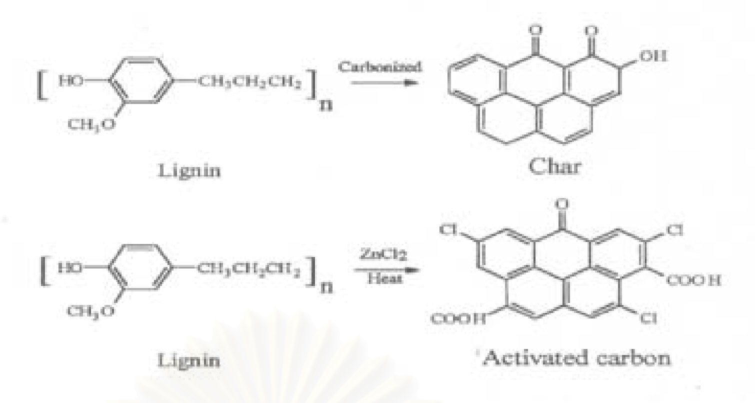

Figure 2.5 Chemical reaction of lignin activated by $ZnCl_2$.

2.6.2.2 Physical activation

Physical activation is the development of porosity by gasification with and oxidizing gas at 700 - 1100 °C . Commonly used gases are carbon dioxide, steam and air. They can be used singly or in combination. Several types of oven can be used in the manufacture of activated carbon, i.e. rotary kilns, multiple heart furnaces and fluidized beds. The type of oven used determines the properties of the activated carbon produced. In general, a decreasing mesoporosity is observed in the order: fluidized bed, multiple hearth furnace and rotary kiln.

To understand the process of "physical" activation it is helpful to use the model of porosity outlined above. This model states that carbons consist of networks of bonded carbon atoms, with a limited extent of ordered structural arrangement, and that porosity is the continuous, interconnected assembly of volume elements between the carbon atoms. It would appear that the ratio of volume element space to carbon atom space is not optimized during normal carbonization procedures. Hence, if carbon atoms can be removed, extremely selectively, from within the carbon particles, then the above ratio will be enhanced (**Figure 2.6**). Because of structural defects and strain energy differences within the defective carbon atom networks, not all carbon atoms have the same reactivity to an oxidizing gas molecule, such as water, carbon dioxide or oxygen.

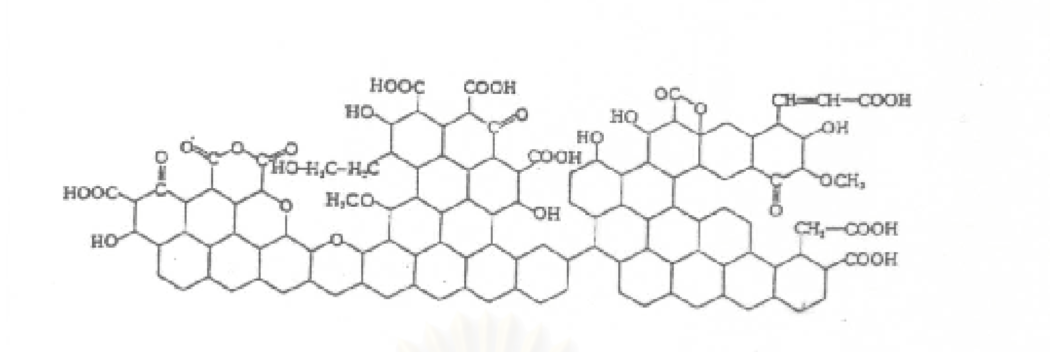

Figure 2.6 Model illustrating the process of physical activation by selective removal of carbon atoms to enhance adsorption capacity.

When gasifying conditions are optimized in terms of oxidizing gas, temperature, flow rate and pressure, an acceptable compromise exists between “selective” burn-off (oxidation) of carbon atoms and “external” burn-off, which is simply removal of carbon material without any increase in porosity. This happens with fast burn- off, e.g. as with oxygen. Thus, the extent of development of porosity and the characteristics of this porosity are a function of:

- the structure of the initial carbon;
- the presence of catalytic inorganic impurities in the carbon;
- the oxidizing gas;
- temperature of gasification;
- pressure of the gas;
- duration of gasification
- particle size of the carbon

Generally, the slower the reaction the more extensive is the development of porosity within the particle. The gas molecule, e.g. carbon dioxide, must penetrate into the interior of the particle to remove a carbon atom from that position. Thus, many carbon atoms within the porous carbon are bypassed during penetration without undergoing reaction or gasification. There are at least two reasons for this: the sensitivity of carbon atom “reactivity” to relative position within the carbon network is critical; also of importance are stereoeffects, i.e. the steam, carbon dioxide or oxygen molecule needs appropriate space to orientate itself for the reaction which leads to gasification. During this process an oxygen atom has to be transferred and bonded to the carbon atom of the network, and the resultant carbon monoxide has subsequently to be “desorbed” from the network. These are extremely complicated processes and may never be understood other than in general terms. In principle, however, it is easy to appreciate how different activation conditions influence the mechanistic detail of carbon atom removal, so creating a wider range of porosities in carbons. This is where activation becomes a matter of experience as well as understanding.

The reaction of carbon with steam and carbon dioxide to remove carbon atoms from the network within solid carbon are follows:

$$C + H_2O \quad = \quad CO + H_2 \qquad \Delta H = +117 \ \text{kJ/ mol}$$

$$C + CO_2 \quad = \quad 2CO \qquad \Delta H = +159 \ \text{kJ/ mol}$$

$$C + CO_2 \quad \Leftrightarrow \quad C\bullet(O) + CO$$

$$C\bullet(O) \quad = \quad C\bullet + CO$$

Where ( ) represents the chemisorbed state.

Steam is the preferred activation gas because the water molecule has smaller dimensions than the carbon dioxide molecule, and consequently the use of steam leads to:

- faster diffusion into the porous network;
- easier access into the micropores;
- a faster reaction rate, i.e. approximately three times than the carbon dioxide reaction at a temperature of 800 °C and a pressure of 10 kPa.

The steam reaction is product inhibited; hydrogen is strongly is adsorbed on the active centers of carbon surface and this reduces rate. In some way, these inhibition reactions also influence the selection of carbon atom removal.

$$C + H_2O \Leftrightarrow C\bullet(H_2O)$$

$$C\bullet(H_2O) \Leftrightarrow C\bullet(O) + H_2 \uparrow$$

$$C + H_2 \Rightarrow C\bullet(H_2)$$

$$C + C\bullet(O) \Rightarrow C\bullet(CO)$$

$$C\bullet(CO) \Rightarrow CO \uparrow$$

The reaction of carbon dioxide with solid carbon is known as Boudouard reaction.The mechanism and kinetics of this reaction have been extensively studied. Activation with carbon dioxide is inhibited by hydrogen and carbon monoxide. The carbon monoxide acts by increasing the rate of the back reaction [$C\bullet(O) + CO = C\bullet + CO_2$]. Rand and Marsh (12) showed that the addition of carbon monoxide to the reacting gas resulted in the development of a better microporous structure in addition to decreasing the rate of gasification. Carbon dioxide activation requires higher temperatures than steam activation and is generally used a mixture of flue gas plus steam. Although pore development is determines the characteristics of the activated carbon produced.

2.7 Chemical nature of the surface of activated carbon

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

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

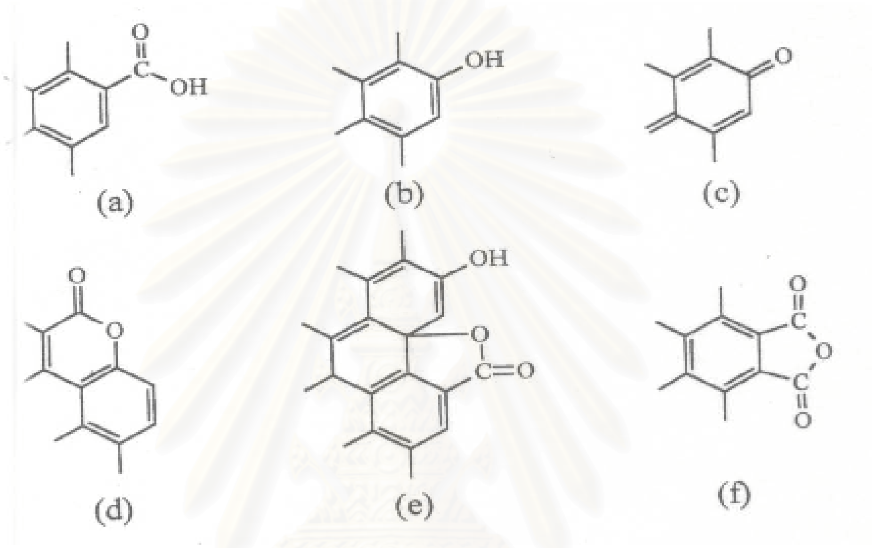

Figure 2.7 Principal types of acidic oxygen surface functional groups : (a) carboxyl, (b) phenolic, (c) quinonoid, (d) normal lactone, (e) fluorescein-type lactone, (f) anhydride originating from neighbouring carboxyl groups.

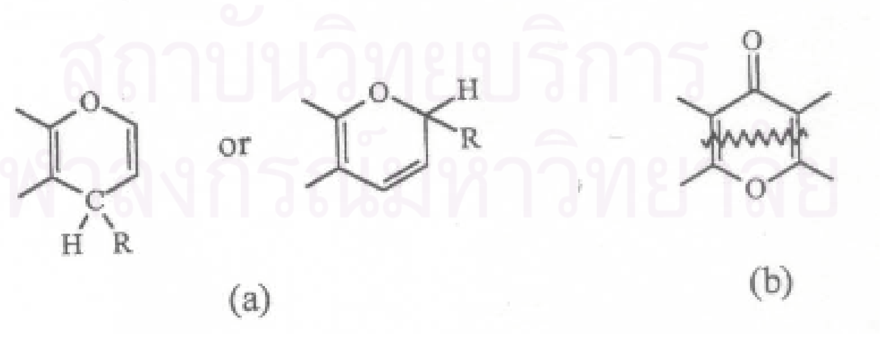

Figure 2.8 Functional groups of basic character : (a) chromene, (b) pyrone-like .

Oxygen surface compounds are usually divided into two main type: functional groups of acidic nature and basic group. The first acidic group is exemplified schematically in **Figure 2.7** the later basic group is much less well-characterized compared with the first. Usually structures corresponding to chromene or pyrone-like structures are illustrated in **Figure 2.8.**

2.8 Literature Reviews

Arriagada, Gercia and Reyes (1994)(15) studied the partial gascification of *Eucalyptus globulus* charcoal, using carbon dioxide and steam as activating agents was studied. The influence of some production variables such as temperature and reaction time on textural were given. *Eucalyptus globulus* chips (5-10 cm in diameter, 30-40 cm in length) were carbonized in a metallic kiln. The carbonization time was 2-3 hr and the yield of charcoal was 23%. The charcoal sieved between 10 and 20 mesh was activated in a vertical fixed bed reactor. The reaction temperature between 800 – 900 °C for 10 – 360 min with flow of the activating agent was 200 cm^3/min (STP) of carbon dioxide or 140 cm^3/min (STP) of steam (100%). The result showed that both activating agents produced microporous activated carbon with a large increase in meso- and macroporosities when steam and high burn-off were used. **Table 2.2** summarizes the textural characteristic of the activated carbon.

Table 2.2 Textural characteristic of the activated carbon (15)

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	874	725	220
	270	994	929	318
	360	1089	936	345
Steam	10	466	471	14
	60	622	690	113

Table 2.2 Textural characteristic of the activated carbon (continued). (15)

Activating agent	Time (min)	Surface area (m^2/g)	IA (mg/g)	MB (mg/g)
Steam	120	778	819	221
	270	1193	968	311

Tancredi *et al*. (1996) (16) prepared activated carbon from eucalyptus wood chars. The results of CO_2, CO_2-O_2 and steam activation were compared. The sawdust of eucalyptus 0.5 – 1.6 mm was first carbonized in a continuous N_2 flow (100 ml/min at STP) in a horizontal tube furnace consisting of a 75 mm diameter quartz tube heated electrically. The carbonization temperature was maintained 400 – 800 ^oC for 2 hr. The chars obtained from this carbonization step were sieved and the 0.5 – 0.8 mm size fraction was activated in the same furnace using CO_2, steam and CO_2-O_2 mixtures as activating agents. Activated carbon was obtained, by CO_2 activation of the 800 ^oC chars with surface area of 780 up to 1190 m^2/g and 810 up to 1190 m^2/g, for steam activation at 800 ^oC. The carbonization step gave rise to a narrow micropore structure and highly developed macroporosity which increased slightly upon CO_2 activation and significantly upon steam activation. This last process led also to widening of micropore size distribution and developed the mesoporosity more than CO_2 activation did. Steam activation appears to have a particularly relevant effect on macroporosity development. As steam had a higher reactivity than CO_2, diffusional limitation could be more significant and would favour gasification in large pores, giving rise to meso- and macroporosity development. This was also consistent with the increase in meso- and macropore volumes with increasing of steam activation temperature. The presence of O_2 accompanying CO_2 in the activating gas small increased the micro-and macroporosity of the carbons, compared with pure CO_2 activation.

Zhonghua Hu et al.(2000) (17) prepared high-surface-area activated carbons by chemical activation of coconut shell with KOH as active agent. The influence of activation parameters on the final products were studied by varying the KOH-to-shell ratio, activation temperature and pre-heat temperatures. The samples were characterized by nitrogen adsorption isotherms at 77 K. The surface area and pore volume of the carbons were estimated by BET, the Langmuir equation and the *t*-plot method. Pre-treatment at 600 °C favored the product with good yield, high surface area and granular form. The BET surface area and pore volume were as high as 2451 m^2 /g and 1.21 cm^3/g, respectively. The activated carbons exhibited a much higher adsorption capacity for phenol, 4-chlorohenol and 4-nitrophenol from aqueous solution than a commercial activated carbon.

Nitcharee Ninlanon (1997) (18) produced activated carbon from Mangrove wood by 2 steps : carbonization and activation using superheated steam and carbon dioxide. The first step is carbonization; variables to be studied were temperature 250-400 °C and time 20-60 min. The optimum condition for carbonization was at 300 °C for 60 min. The characteristics of char were found to be: % yield = 38.07, % fixed carbon = 71.44, % volatile matter = 23.02 and % ash = 5.54. The second step is to activate the char by using superheated steam and carbon dioxide. The variables were temperature 700-850 °C , time 30, 60, 90 and 120 min. and sizes of particle < 0.355, 0.355-0.60, 0.60-1.18, 1.18-2.36, 2.36-4.75 mm. It was found that the optimum condition for activation was at 850 °C for 60 min. and 0.60-1.18 mm size of particles. The quantity of air and carbon dioxide were 5l/min. at 30 °C, 1 atm with excess superheated steam, respectively. The resulting characteristics were 27.47 % yield, BET surface area 639.74 m^2/g, macropores surface area 156.50 m^2/g, micropores surface area 483.24 m^2/g, Iodine adsorption number 675.14 mg/g and methylene blue adsorption number 254.73 mg/g.. It was also found that the capabilities of the activated carbon on colour adsorption of dichromate ion were 66.23 and 59.52 mg/g at pH 1-2 respectively.

D. Lozano-Castallo, et al. (part1) (2001) (19) used Spanish anthracite for the preparation of activated carbon by KOH. The results indicated that raw material is promising for that proposes. This work was extended and effect of different preparation variable on the final porous texture was discussed, such as KOH/anthracite ratio, heating rate, and carbonization temperature and carbonization time. Among those different variables studied, the KOH/anthracite ratio seems to be the most important one. In addition, this study introduces an investigation of nitrogen flow rate, showing that this variable has very important effect on porosity development. The study confirms that the raw material used is appropriate for the preparation of activated carbon in a single stage pyrolysis process. The paper choice of the preparation conditions allows use to produce microporous activated carbons with a micropore volume up to 1.45 cm^3/g and BET surface area of 3290 m^2/g.

D. Lozano-Castallo, et al. (part2) (2001) (20) continued of previous one (activation with KOH) analyzing the development of porosity of a Spanish anthracite by chemical activation with NaOH. The preparation method has been optimized through the analysis of diverse experimental variables. Among them, activating agent/coal ratio, drying process, method of mixing of the activating agent and coal, nitrogen flow during pyrolysis and mineral matter content of the coal, have been studied. The results obtained confirm the importance of the activating agent to coal ratio and the flow of gas during carbonisation on the development of porosity. In addition, it shows that chemical activation with NaOH can be successfully used to develop activated carbons with high surface area and micropore volumes (i.e., up to 2700 m^2/g and 1 cm^3/g). Comparing chemical activation using an impregnation method and physical mixing, they concluded that physical mixing of NaOH and coal, which is a very easy preparation method, renders the best result. Therefore physical mixing has been also applied in this work to KOH with rather interesting results. Although impregnation produces a higher development of porosity for KOH, activated carbons with high micropore volumes can be synthesised through a much simpler method. Physical mixing produces larger pore volumes by KOH activation than by NaOH activation.

Thawatchai Tuncharoensap (2001) (21) produced activated carbon from Thai lignite. This research was comparison of the properties of activated carbon, which was chemical and physical activation. The first step of an experimental process was carbonization. The temperature and time were investigated. It was found that the optimum condition was at 450 °C for 45 min. The second step was to activate the char, which can be divided into two methods. For the first method, the potassium hydroxide solution was used in the chemical activation. The considered variables were ratio of reagent: char, temperature, reaction time and particle size. The optimum condition was 0.7: 1 of ratio reagent : char, temperature at 800 °C, reaction time 4 hours and particle size range between 0.50 – 0.85 mm., which the properties of obtained activated carbon was a yield , 50.87 %, bulk edensity0.318 g/cc, 14.61 % ash, 846 mg/g of iodine number, 229 mg/g methylene blue number and

1292 m^2/g surface area. Second method was physical activation that gave the suitable variables at 850 ^{o}C, 4 hours activation time and particle size range from 0.50-0.85 mm, which was the optimum condition. The obtained activated carbon was 60.42 % yield, 0.544 g/cc bulk density, 26.87% ash, 242 mg/g iodine number and 41 mg/g methylene blue number. The comparison of the two methods showed that the property of activated carbon from chemical activation is better and not much different from the commercial grade.

CHAPTER III

EXPERIMENTAL

3.1 Raw material

This experiment used Para wood for the production of activated carbon by oxidizing gas and alkaline solution activation. The Para wood was carbonized and sieved to three different particle sizes of 0.06-1.18, 1.18-2.36 and 2.36-4.75 mm. Para wood particle size used was 1.18-2.36 mm only. The pictures of Para wood and Para wood char are shown in **Figure 3.1** respectively.

(A) (B)

Figure 3.1 (A) Para wood (raw material), (B) Para wood char.

3.2 Chemicals

1. Hydrochloric acid, concentrated (HCl)
2. Iodine, (I_2)
3. Potassium iodine, (KI)
4. Potassium iodate, (KIO_3)
5. Sodium thiosulfate, ($Na_2S_2O_3\ 5H_2O$)
6. Sodium carbonate, (NA_2CO_3)
7. Starch, soluble potato
8. Potassium phosphate, (KH_2PO_4)
9. Methylene blue, ($C_{16}H_{18}N_3SCl\ 3H_2O$)
10. Sodium phosphate, (NA_2HPO_4)
11. Potassium hydroxide (KOH)
12. Sodium hydroxide (NaOH)

3.3 Apparatus

1. Motor grinder : type RM 100, Retch, Germany.
2. Laboratory sieve tray: stainless steel sizes 850 μm, 1.18 mm, 2.36 mm and 4.75 mm, Endecotts, England., shown in **Figure 3.2**
3. Vertical activator 0 - 1200 °C
4. Reactor: 0.02 m of diameter, 0.50 m long made from SS. 304., shown in **Figure 3.3**
5. Muffle furnace : type ESF 12/23 (0-1200 °C), Carbolite, England.
6. Surface area analyzer: Micromertrics FlowSorb 2300
7. Oven : (0-250 °C) WT binder, Germany.
8. Scanning Electron Microscope (SEM) : JSM-5410 LV
9. Tube furnace : type 21100 (0-1200 °C), Thermolyne Corporation. USA., shown in **Figure 3.4**
10. Crucible 20 and 120 ml

11. Horizontal shaker
12. Bubble flow
13. Desicator
14. Regulator

Figure 3.2 Laboratory sieve tray

Figure 3.3 Reactor

Figure 3.4 Tube furnace

3.4 Procedures

3.4.1 Carbonization of Para wood

The optimum temperature and time for carbonization of Para wood were studied at 350, 400, 450 and 500 ^{o}C for the duration of 45, 60, 90 and 120 min. The procedures started sample about 70g (by weight) in a crucible. Next, muffle furnace was heated at the final temperature as 350, 400, 450 and 500 ^{o}C and put the sample for 45, 60, 90 and 120 min, respectively. Finally, % yield, % ash, bulk density, % volatile matter and % fixed carbon of products were analyzed followed ASTM.

3.4.2 Activation of Para wood char

3.4.2.1 Activation by oxidizing gas

The variables, which have an effect on the activation such as: temperature, activation times, sizes of char were studied in order to determine the optimum conditions. Experimental scheme of the production of activated carbon from Para wood was shown in **Figure 3.5.** The procedure were described as follows:

3.4.2.1.1 The effect of activation temperature. Four different temperatures were studied in this work for activation. They were 750, 800, 850 and 900 ^{o}C. 9 g of Para wood with particle size of 1.18-2.36 mm was loaded into a stainless tubular reactor. Then the reactor was passed with CO_2, steam and air at the bottom. Then CO_2 was allowed to flow through from the bottom to the top at the flow rate of 500 ml/min, steam 10 g/min and air 5 ml/min. Secondly, the reactor was heated to the desired temperature to vary at 750, 800, 850 and 900 ^{o}C . The CO_2, steam and air were charged continuously on, passing up through the reactor for each fixed temperature and for 3 hrs of reaction time. Finally, bulk density, iodine number, methylene blue number and B.E.T. surface area characterized the product.

3.4.2.1.2 The effect of activation time. Different activation times of 1, 2 and 3 hrs were studied for activation. 9 g of Para wood char with particle size of 1.18-2.36 mm was loaded into the reactor. The procedure of operation was the same as the earlier mentioned experiment, Then the reactor was passed with CO_2, steam and air at the bottom. Then CO_2 was allowed to flow through from the bottom to the top at the flow rate of CO_2 500 ml/min, steam 10 g/min and air 5 ml/min. Secondly, the reactor was heated until the temperature was increasing and being fixed at the temperature 800 ^{o}C. The CO_2, steam and air were continued on, passing up through the reactor for varying reaction time of 1, 2 and 3 hrs. Finally, bulk density, iodine number and methylene blue number characterized the product.

3.4.2.1.3 The effect of size of Para wood char for activation. The sizes of Para wood char of 0.06 - 1.18, 1.18 - 2.36 and 2.36 - 4.75 mm were studied to get the

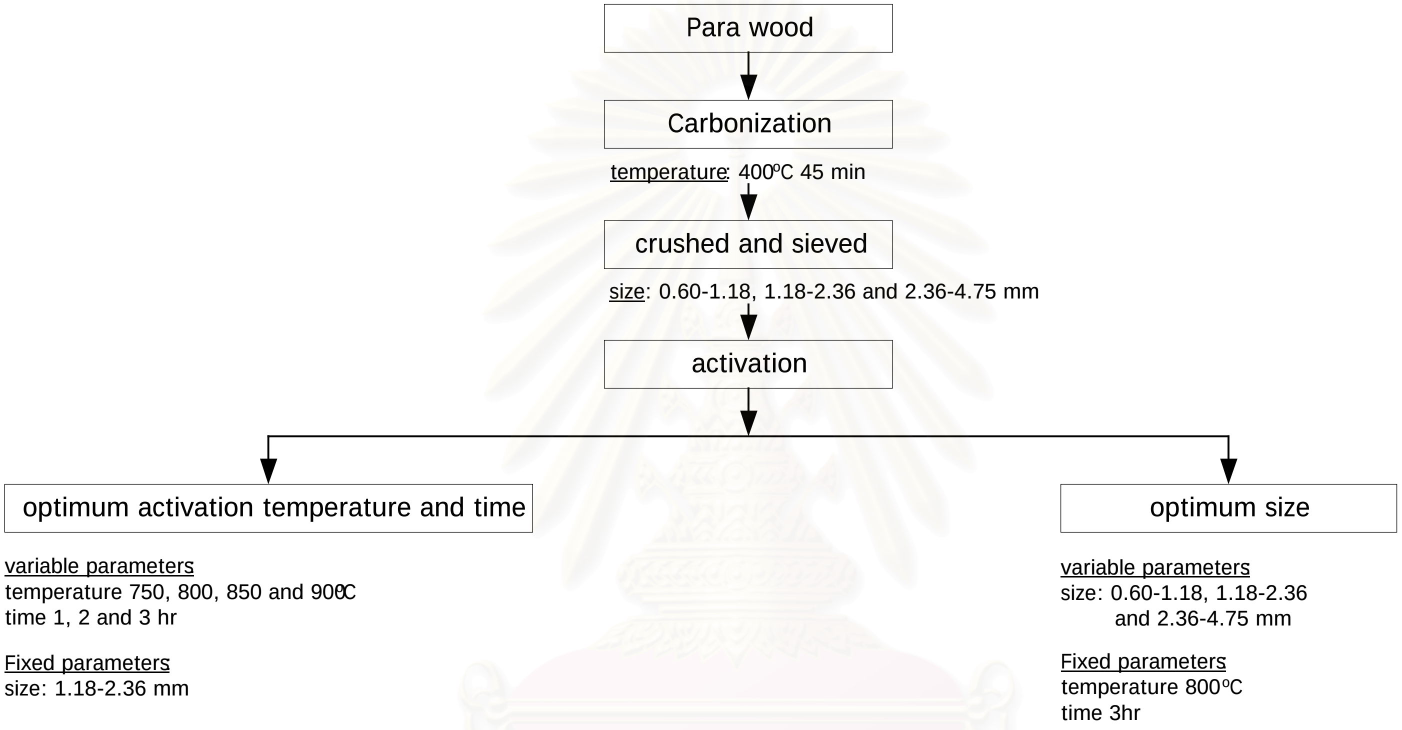

Figure 3.5 Experiment scheme of the production of activated carbon from Para wood by oxidizing gas in a fixed bed reactor

optimum size for preparation of activated carbon. 9 g of Para wood char was loaded into a reactor. Then the reactor was passed with CO_2, steam and air at the bottom. Then gas was allowed to flow through from the bottom to the top at the flow rate of CO_2 500 ml/min, steam 10 g/min and air 5 ml/min. Secondly, the reactor was heated until the temperature was increasing and being fixed at the temperature 800 ^{o}C. The CO_2, steam and air were continued on, passing up though the tube reactor for 3 hr. Finally, the product of each experiment was characterized by bulk density, iodine number and methylene blue.

3.4.2.2 Activation by alkaline solution

The variables, which have an effect on the activation such as: temperature, activation time, concentration of KOH, size of char and alkaline solution that used for activation were studied in order to determine the optimum conditions. Experimental schemes of the production of activated carbon from Para wood were shown in **Figure 3.6** respectively. The procedures were described as follows:

3.4.2.2.1 The effect of concentrations of potassium hydroxide activation. The different concentrations of KOH at char : KOH ratio 1:1, 3.1, 5:1, 7:1 and 10:1 by weight were studied to determine the optimum concentration for soaking for preparation of activated carbon. Firstly, 9 g of Para wood (1.18 – 2.36 mm of particle size) was soaked in different concentrations of KOH. The operation was carried out the same as the earlier mentioned experiment. The tube reactor was connected to a nitrogen tank. Secondly, the reactor was heated until the temperature in the tube rising and being fixed at the final temperature 700 ^{o}C. The nitrogen gas was continued on, passing up through the tube reactor for 3 hrs of each experiment. Finally, the product was characterized by bulk density, iodine number, methylene blue number, B.E.T. surface area.

3.4.2.2.2 The effect of temperature for activation. Three different temperatures were studied in this work for activation. They were 500, 600 and 700 ^{o}C.

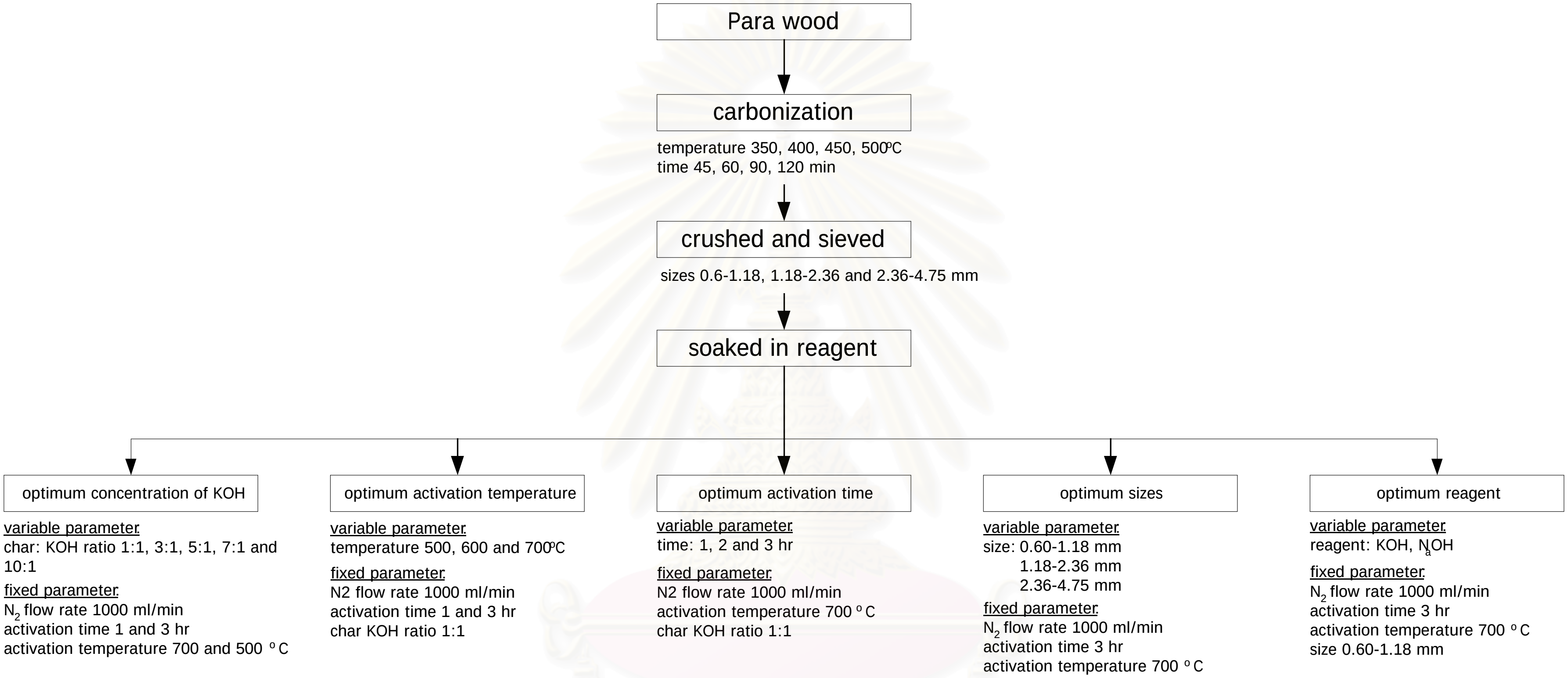

Figure 3.6 Experiment scheme of the production of activated carbon from Para wood by alkaline solution in fixed bed reactor.

Firstly, the sample 9 g of Para wood with particle size of 1.18 - 2.36 mm were soaked in char: KOH ratio 1:1, then dried and loaded into a stainless tubular reactor. Then the reactor was passed with nitrogen gas at the bottom. The nitrogen gas was then allowed to flow through from the bottom to the top at the flow rate of 1000 ml/min. Secondly, the reactor was heated to the desired temperature to vary at 500, 600 and 700 ^{o}C. The nitrogen gas was continued on, passing up through the reactor for each fixed temperature and for 3 hrs of reaction time. Finally, the product was characterized by bulk density, iodine number, methylene blue number, B.E.T. surface area.

3.4.2.2.3 The effect of time for activation. Different reaction times of 1, 2 and 3 hr were studied for activation. Firstly, 9 g of Para wood char with particle size of 1.18-2.36 mm were soaked in char : KOH ratio 1:1, then dried and loaded into a stainless tubular reactor. The procedure of operation was the same as the former experiment. The reactor was passed with nitrogen gas at the bottom. The nitrogen gas was then allowed to flow through from the bottom to the top at the flow rate of 1000 ml/min. Secondly, the reactor was heated until the temperature was increased and being fixed at the temperature 700 ^{o}C. The nitrogen gas was continued on, passing up through the reactor for varying reaction time of 1, 2 and 3 hrs. Finally, the product was characterized by bulk density, iodine number, methylene blue number, B.E.T. surface area.

3.4.2.2.4 The effect of size of Para wood char for activation. The sizes of Para wood char of 0.06 - 1.18, 1.18 - 2.36 and 2.36 - 4.75 mm were studied to get the optimum size for preparation of activated carbon. 9 g of Para wood char was loaded into reactor for varying particle size of 0.06 – 1.18, 1.18 - 2.36 and 2.36 – 4.75 mm were soaked in char : KOH ratio 1:1, then dried and loaded into a stainless tubular reactor. The procedure of operation was the same as the former experiment. The reactor was passed with nitrogen gas at the bottom. The nitrogen gas was then allowed to flow through from the bottom to the top at the flow rate of 1000 ml/min. Secondly, the reactor was heated until the temperature was increasing and being fixed at the temperature 700 ^{o}C. The nitrogen gas was continued on, passing up through. The tube reactor for 3 hrs. Finally, the product of each experiment was characterized by bulk density, iodine number, methylene blue, B.E.T. surface area.

3.4.2.2.5 The effect of reagent for alkaline solution activation. The two different alkalines as KOH and NaOH were studied to determine the effect of activation. 9 g of Para wood char (0.60-1.18 mm of particle size) was soaked in different alkalines at char: alkaline ratio of 1:1. The activation was proceeded as the former experiment. The tube reactor was connected to N_2 tank. Secondly, the bed was heated until the temperature in the tube increased and being fixed at the final temperature 700 °C. The nitrogen gas was continued on, passing up through the tube reactor for 3 hr of each experiment. Finally, the product was characterized by bulk density, iodine number, methylene blue number, B.E.T. surface area.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Carbonization

Para wood was carbonized before activation with oxidizing gas and alkaline solution. The carbonization was carried out in a muffle furnace. The studied condition was temperature range of 350 to 500 °C and each temperature being varied carbonization time from 45 to 120 minutes. The proximate analysis of Para wood char is presented in **Table 4.1**

Table 4.1 Proximate analysis of Para wood char at different temperatures and times.

Temp (°C)	Time (min)	Y(%wt)	M(%wt)	Ash(%wt)	VM(%wt)	FC(%wt)
350	45	31.94	1.50	2.87	34.12	61.51
	60	32.83	1.95	1.22	33.86	62.96
	90	30.36	1.67	3.00	33.20	62.13
	120	28.96	1.99	3.38	31.05	63.57
400	**45**	**27.51**	**1.32**	**2.32**	**25.90**	**70.46**
	60	26.77	1.54	3.22	23.81	71.43
	90	26.33	1.28	4.15	25.62	68.95
	120	26.14	1.85	3.66	25.72	68.76
450	45	23.92	1.09	4.33	21.99	72.59
	60	24.92	1.53	3.87	21.60	72.99
	90	24.12	1.88	3.94	22.08	72.09
	120	22.92	1.87	2.66	18.81	76.66
500	45	23.53	1.76	4.66	17.42	76.15
	60	22.18	1.85	4.04	14.93	79.18
	90	22.35	2.04	4.20	17.20	76.55
	120	20.83	1.99	4.05	15.90	78.06

After considered volatile matter, fixed carbon and yield in **Table 4.1**, the optimum condition for carbonization of Para wood was 400 °C for 45 min. because the characteristic of Para wood char at this condition contained 20-25 % volatile matter (22) which was appropriated for activation. The carbonized Para woods, was 27.51 % yield, 2.3156 % ash and 70.4643 % fixed carbon. The Para wood char prepared at this condition would be used in activation steps.

4.2 Results and discussion of the experiments

4.2.1 Activation by oxidizing gas

4.2.1.1 The effect of activation temperature

The amount of 9 g of 1.18 – 2.36 mm of Para wood was used in each batch. The reactor was heated to the final temperature of 750, 800, 850 and 900 °C before the Para wood sample was charged into the reactor. After charging, the excess steam was passing up through at a fixed flow of CO_2 500 ml/min, steam10 g/min and air 5 ml/min for 1, 2 and 3 hrs. The results of this experiment are shown in **Table 4.2 and Figures 4.1 – 4.5.**

Table 4.2 Characteristics of activated carbon from Para wood at different temperatures and times (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

NO.	Temp (^oC)	Time (hr.)	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)
1	750	1	50.39	0.24	5.73	96	410
2	750	2	52.11	0.23	5.12	121	463
3	750	3	49.12	0.22	5.48	119	480
4	800	1	48.48	0.22	6.94	109	482
5	800	2	47.37	0.22	6.45	126	479
6	**800**	**3**	**44.44**	**0.21**	**7.33**	**154**	**512**
7	850	1	46.20	0.20	9.61	110	481
8	850	2	40.35	0.20	8.37	160	520
9	850	3	39.77	0.19	9.01	143	505
10	900	1	36.26	0.19	13.12	120	475
11	900	2	35.09	0.19	10.96	125	421
12	900	3	29.24	0.18	12.04	127	449

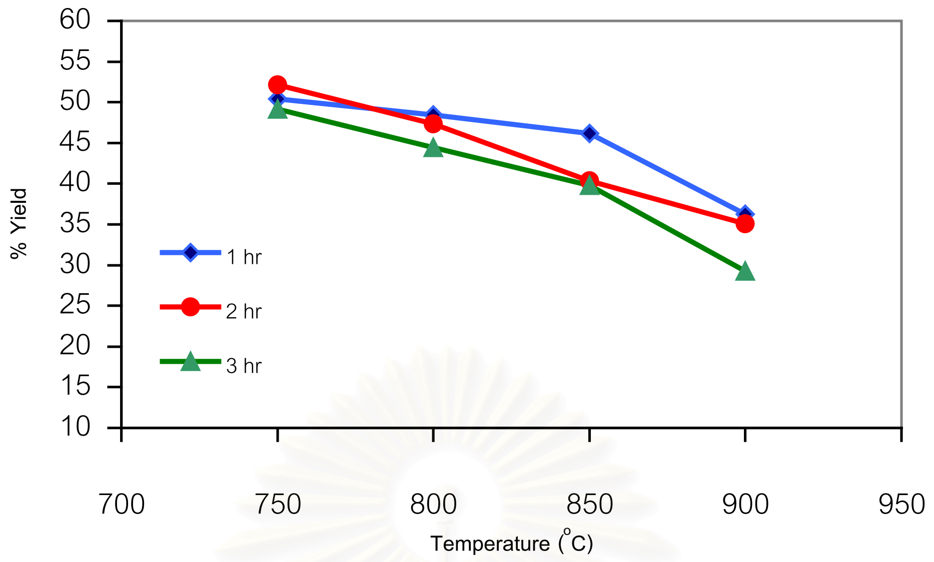

Figure 4.1 Effect of activation temperature on % yield at different times (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

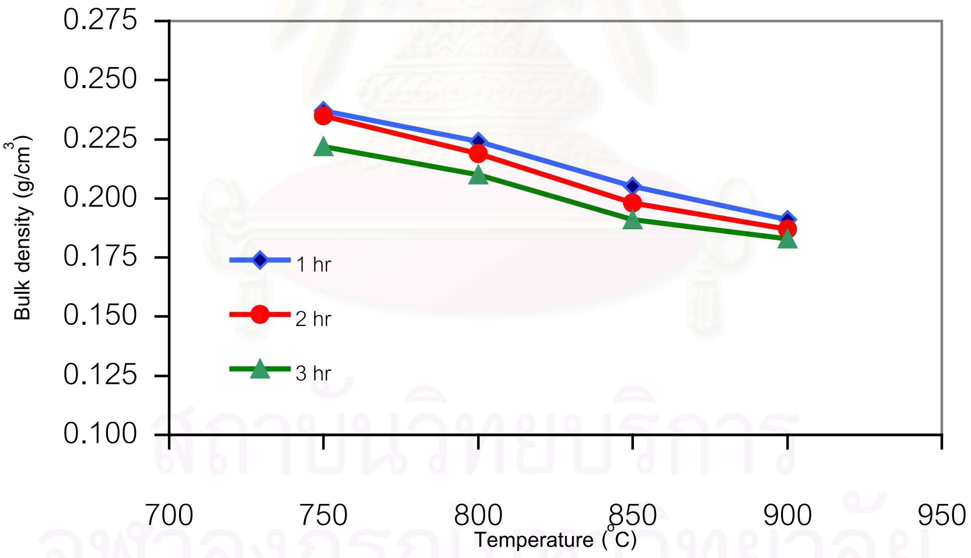

Figure 4.2 Effect of activation temperature on bulk density at different times (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

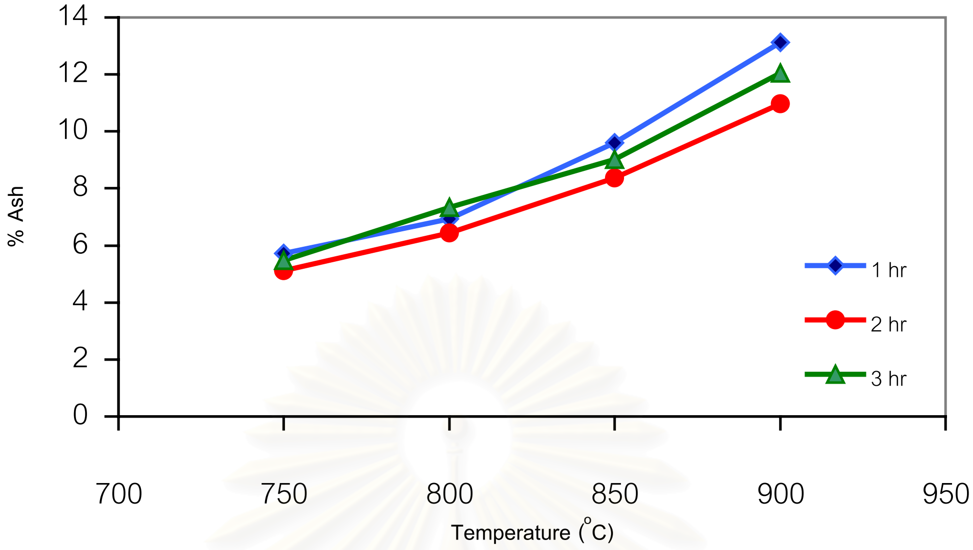

Figure 4.3 Effect of activation temperature on % ash at different times (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

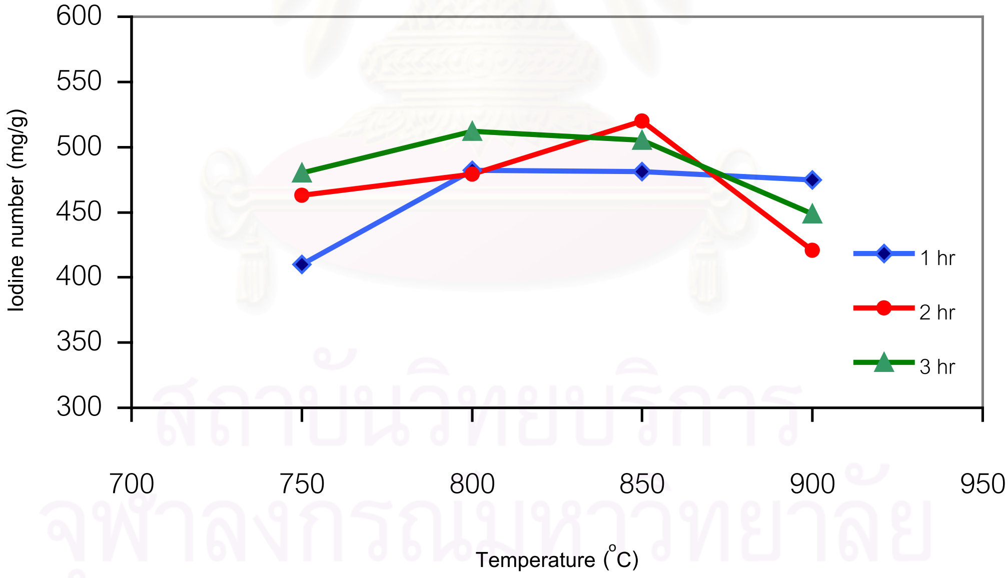

Figure 4.4 Effect of activation temperature on iodine number at different times (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

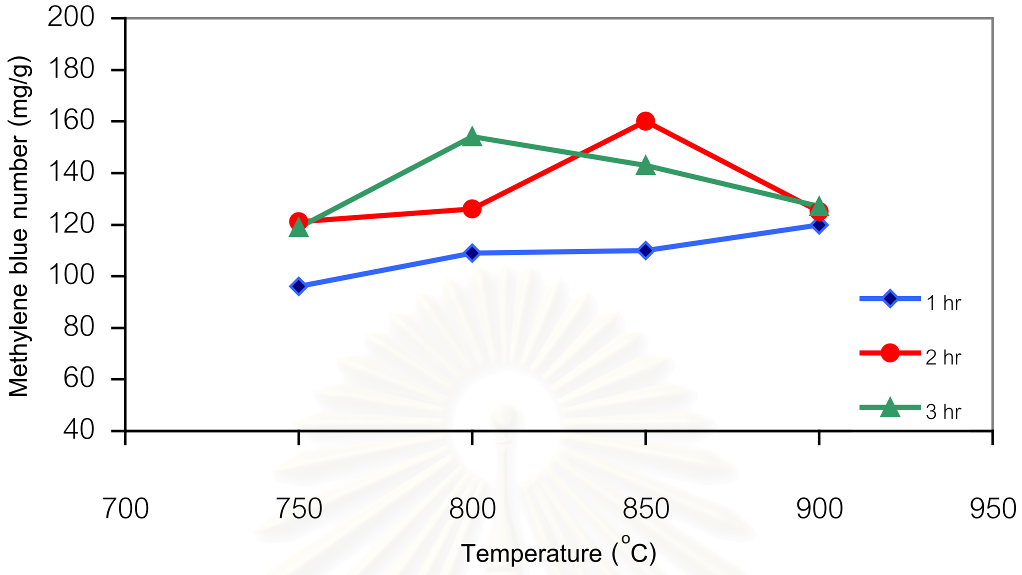

Figure 4.5 Effect of activation temperature on methylene blue number at different times (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

From **Table 4.2** and **Figures 4.1-4.2**, in temperature range of 750, 800, 850 and 900 °C, for 1-3 hr the % yield and bulk density are decreased. At high temperature, steam and carbon dioxide relatively better than at low temperature attacked Para wood char. The changes in the yielding % Para wood were varied about 9.5 % from 750 to 800 °C , 34.2 % from 800 to 900 °C. So % yield and bulk density are decreased, in the opposition of the % ash of the product (**Figure 4.3**). The % ash in the first stage (750-800 °C) is increasing slowly because only the volatile matter at the surface is diffused. Hence the % ash is rather constant. When time increases to 3 hr, the % ash would increase quickly. But when the temperature increases from 800 - 900 °C for 1 and 2 hr, the % ash in this stage would increase faster than the % ash in the first stage (750 - 800 °C). This is because, most of the matter is diffused in the first stage in conjunction with high partial combustion by air. The % ash obtained at 800 - 900 °C for 3 hr increases the fastest of all. These results show that timing has effected the change of the % ash at the low activation temperature.

From **Table 4.2**, with an increasing temperature from 750-800 °C for 1, 2 and 3 hr, the bulk density is decreasing (**Figure 4.2**). This is because at high temperature, porosity is highly developed. The bulk density remains fairly constant while the temperature raises up from 750-800 °C. At the same time, there is a small increase of iodine number. However the bulk density decreases quickly, whereas the temperature increases from 800-900 °C. This phenomenon happens as a result of high development of porosity, which can be seen from increasing of the iodine number and methylene blue number. Changing in bulk density of Para wood varies about 5.48% from 750 to 800 °C, 14.73% % from 800 to 900 °C as shown in **Table 4.2**.

Figures 4.4 – 4.5 show that when the activation temperature raising up the iodine number and methylene blue number are also increasing. At the first stage (750-800 °C), iodine number increases quickly because the diffusion of volatile matter hinders the penetration of steam. The most of volatile matter is diffused from granules (**Table 4.2**) then made high development of porosity but at 800-850 °C. The iodine number increased slowly and some time decreased because at high temperature micropores would break to mesopores and macropores and thus reducing the iodine number and methylene blue number. The optimum temperature for activation by oxidizing gas is 800 °C because this level contains high iodine number, high methylene blue number but moderate temperature.

4.2.1.2 The effect of activation time

Para wood, 1.18-2.36 mm in particle size and 9 g in weight were used in each batch. The reactor had been heated up to the final temperature of 750, 800, 850 and 900 °C before the Para wood sample was charged into the reactor. After charging, the excess steam was passing up through at a fixed flow of CO_2 500 ml/min, steam10 g/min and air 5 ml/min for 1, 2 and 3 hr. The result of this experiment are shown in **Table 4.2** and **Figures 4.6 - 4.10**.

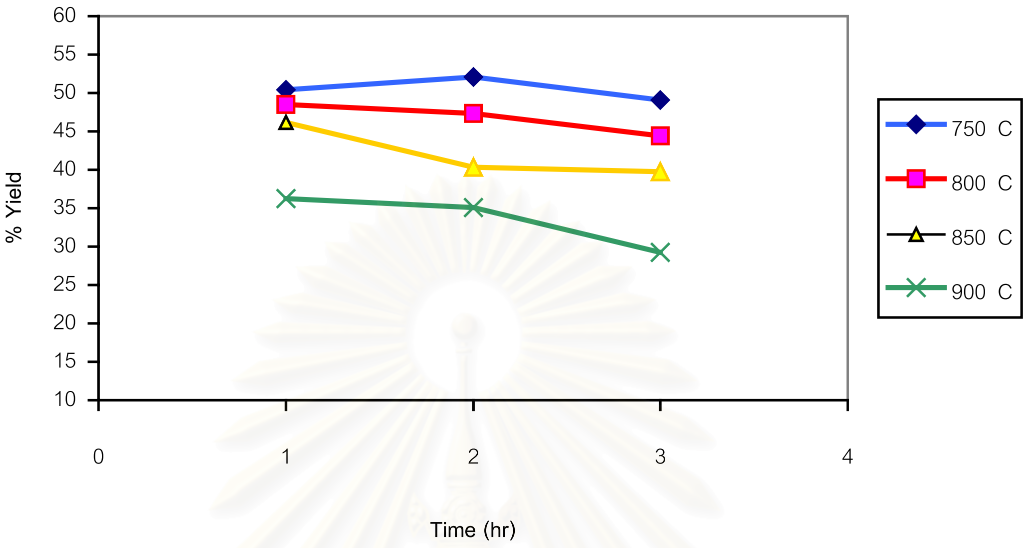

Figure 4.6 Effect of activation time on % yield at different temperatures (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

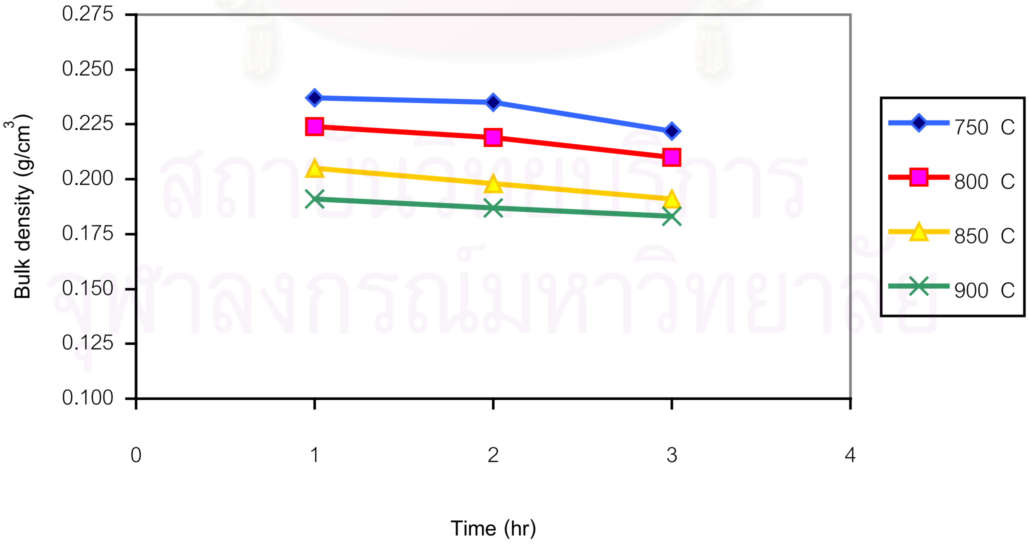

Figure 4.7 Effect of activation time on bulk density at different temperatures (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

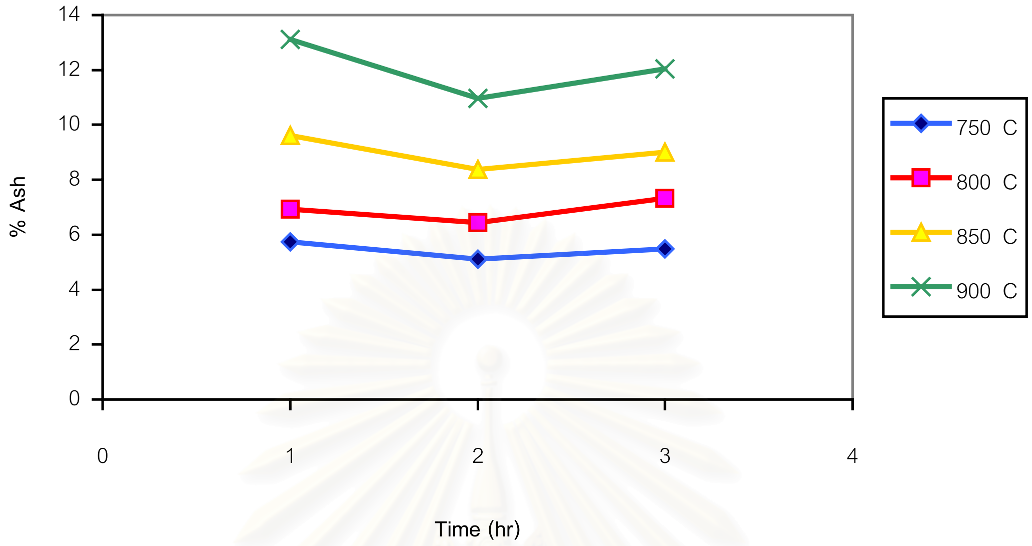

Figure 4.8 Effect of activation time on % ash at different temperatures (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

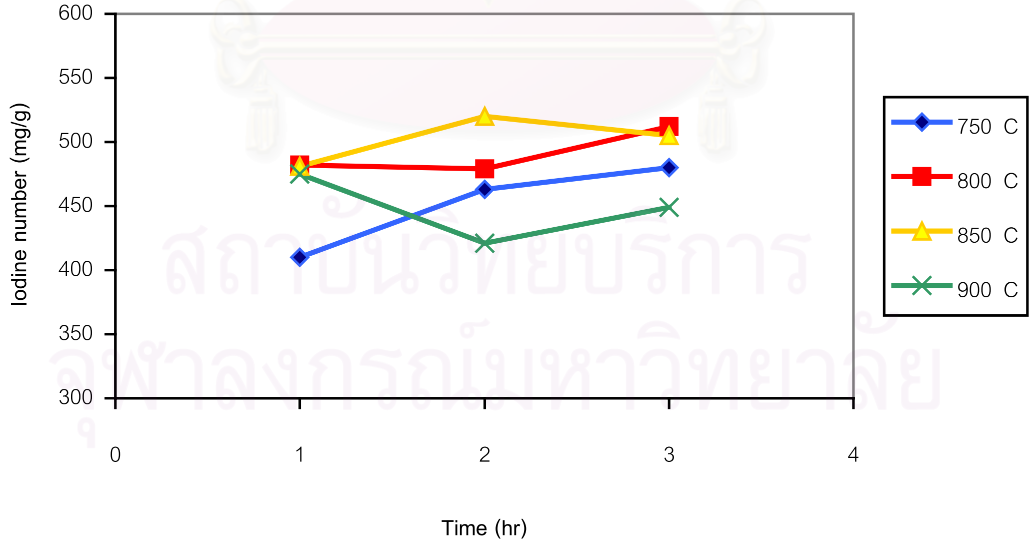

Figure 4.9 Effect of activation time on iodine number at different temperatures (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

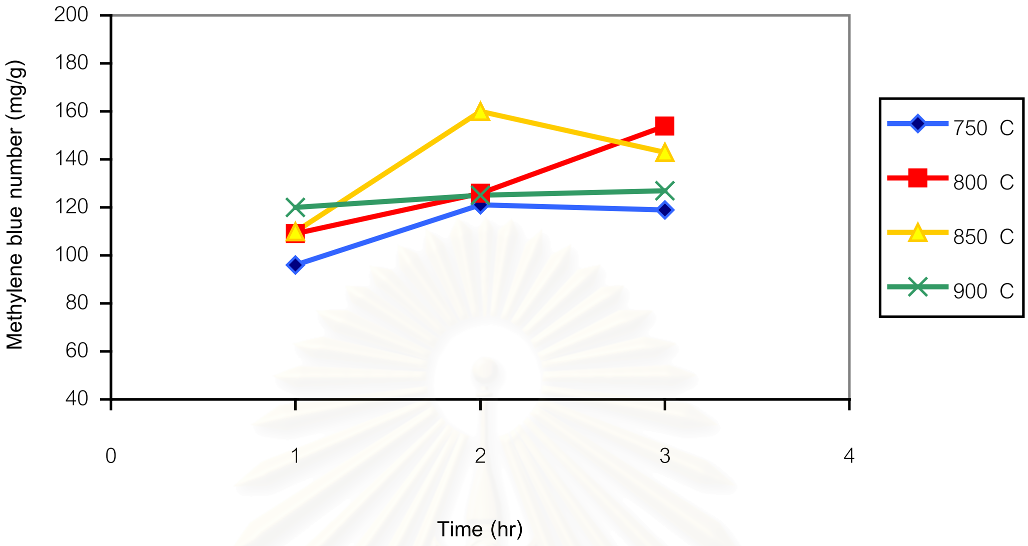

Figure 4.10 Effect of activation time on methylene blue number at different temperatures (size 1.18 – 2.36 mm, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

Table 4.2 and **Figure 4.6**, ranging from 1 to 3 hr at 750, 800, 850 and 900 °C, % yield decreased because of loss of volatile matter and partial combustion with air. Therefore, the % yield decreases which is the opposite of the % ash of the product that being increased (**Figure 4.8**). The % ash in the first stage (1-2 hr) increases slowly because only the volatile matter at the surface diffuses. But when time increases to 3 hr, the % ash increases quickly. Because most of the matter is diffused in the first stage and air helps high partial combustion occurring.

Figure 4.9, showed the iodine number with the time range of 1-2 hr increases lower than the range of 2-3 hr. Because of at the range of 1-2 hr, the diffusion of volatile matter hinders the penetration of steam into the surface of Para wood (**Table 4.2**). The pores, nevertheless, are less developed at the time range of 2-3 hr. The iodine number and the methylene blue number are increasing in the rates that are comparatively the same, because most of volatile matter is diffusing in the first stage. The steam penetrates easily with the surface of Para wood, therefore, the porosity development increases. The high development of porosity makes the bulk density decreased in the time range of 1-3 hr at 750, 800, 850, and 900 °C (**Figure 4.7**). The changing % bulk density is shown in **Table 4.2.**

Having the maximum of iodine number and methylene blue number, the optimum condition should be 850 °C at 2 hr. But the % yield in this condition is lower than that of 800 °C for 3 hr. However, iodine number and methylene blue number are found with no difference. Thus, the optimum time is 3 hr at 800 C. It saves more resources for activation than 850 °C for 2 hr.

The optimum condition for activation by oxidizing was 800 °C for 3 hr. The characteristics of activated carbon with the yield of 44.44 % represent at bulk density of 0.21 g/cm^3, ash of 7.33 %, iodine number of 512 mg/g and methylene blue number of 154 mg/g. This optimum condition will be continued for the further study of other variables.

4.2.1.3 The effect of size of the Para wood char

Three size of Para wood were used to study the optimum of size. They were 0.60-1.18, 1.18-2.36 and 2.36-4.75 mm. Approximately 9 g of each Para wood sample was treated at 800 °C for 3 hr with carbon dioxide 500 ml/min, steam 10 g/min and air 5 ml/min in the reactor. The results are shown in **Table 4.3** and **Figures 4.11-4.15.**

Table 4.3 Effect of size on properties of activated carbon that activated by oxidizing gas

Size (mm.)	Temp °C	Time Hr	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)
0.60-1.18	**800**	**3**	**43.80**	**0.20**	**7.86**	**168**	**523**
1.18-2.36	800	3	44.44	0.21	7.33	154	512
2.36-4.75	800	3	46.25	0.22	6.98	141	483

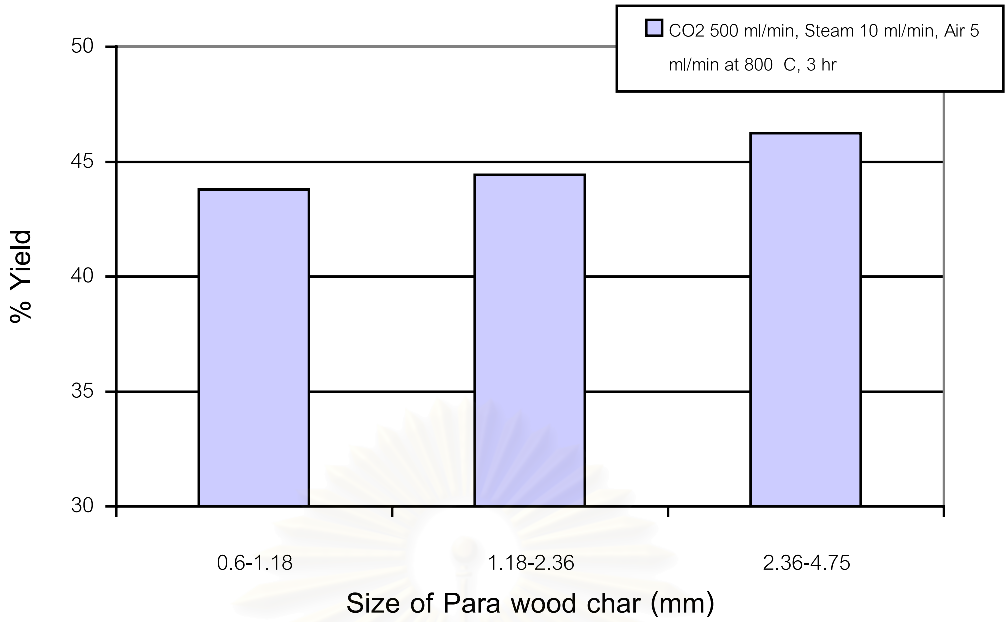

Figure 4.11 Effect of size of Para wood char on % yield (at 800 °C, 3 hr, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

Figure 4.12 Effect of size of Para wood char on bulk density (at 800 °C, 3 hr, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

Figure 4.13 Effect of size of Para wood char on % ash (at 800 °C, 3 hr, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

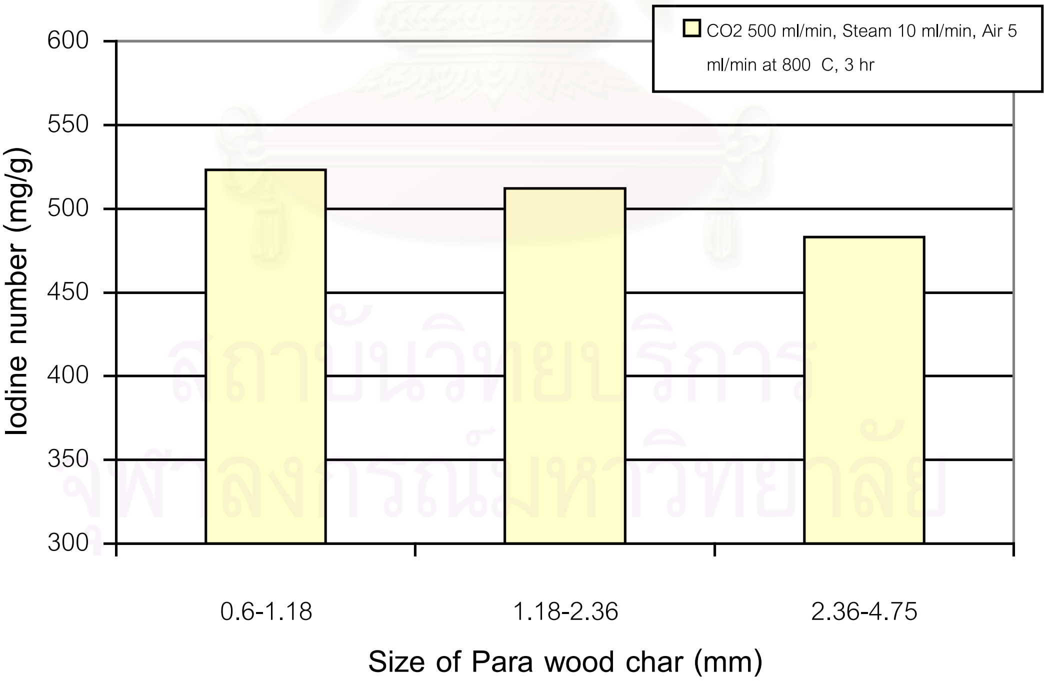

Figure 4.14 Effect of size of Para wood char on iodine number (at 800 °C , 3 hr, 9 g,CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

Figure 4.15 Effect of size of Para wood char on methylene blue number (at 800 °C, 3 hr, 9 g, CO_2 500 ml/min, steam 10 g/min and air 5 ml/min).

From **Table 4.3** and **Figures 4.11-4.12**, the % yield and bulk density of small Para wood (0.60 – 1.18 mm in size) are lowest because the small size Para wood pack more tightly in the reactor. So, the steam is difficult to penetrate in the surface. Furthermore, small particles burn out early due to faster reaction rates. This results in pore coalescence and reducing the iodine number as comparing with large particles.

For the particle sizes of 1.18-2.36 and 2.36 - 4.75 mm. the iodine number and methylene blue number decrease because these particles pack very loosly, so the steam passes suddenly and could not contact completely with the surface of Para wood particles.

The experimental results showed that the optimum size of Para wood char for activation was 0.60-1.18 mm because the characteristic of activated carbon gave the highest iodine number and methylene blue number. Properties were at % yield of 43.80 %, bulk density of 0.20 g/cm^3, 7.86 % ash, iodine number of 523 mg/g, methylene blue number of 168 mg/g and B.E.T. surface area of 437.64 m^2/g.

4.2.2 Activation by alkaline solution

4.2.2.1 The effect of concentration of potassium hydroxide activation

The concentration of potassium hydroxide solution at char: KOH ratio (by weight) 1:1, 3:1, 5:1, 7:1 and 10:1 were prepared. The char from Para wood were soaked by these different solutions for studying the influence of concentration of solution on characteristics of prepared activated carbon. 9 g of 1.18-2.36 mm of Para wood char were carried out at 500 and 700 °C for 1 and 3 hr by passing nitrogen gas though the reactor. The results of this experiment were shown in **Tables 4.4-4.7** and **Figures 4.16-4.20.**

Table 4.4 Effect of KOH concentration (500°C, 1 hr, N_2 flow rate 1000 ml/min).

Concentration (char : KOH (w/w))	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
1:1	68.76	0.19	3.76	98	416	85.54
3:1	70.1	0.20	3.23	92	312	N/A
5:1	69.76	0.20	4.13	71	302	N/A
7:1	70.61	0.21	5.23	57	288	N/A
10:1	71.35	0.21	3.69	26	203	N/A

Table 4.5 Effect of KOH concentration (500°C, 3 hr, N_2 flow rate 1000 ml/min).

Concentration (char :KOH (w/w))	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m2/g)
1:1	64.62	0.18	4.14	110	471	N/A
3:1	65.47	0.18	5.68	81	406	N/A
5:1	71.98	0.20	5.39	83	414	N/A
7:1	71.61	0.20	4.27	49	296	N/A
10:1	73.56	0.21	4.12	51	210	N/A

Table 4.6 Effect of KOH Concentration (700°C, 1 hr, N_2 flow rate 1000ml/min).

Concentration (char :KOH (w/w))	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T (m^2/g)
1:1	60.26	0.17	3.27	113	652	546.41
3:1	64.15	0.19	3.65	67	398	N/A
5:1	68.45	0.19	4.32	84	305	N/A
7:1	70.5	0.20	3.98	76	314	N/A
10:1	73.22	0.21	3.66	43	268	N/A

Table 4.7 Effect of KOH Concentration (700°C, 3 hr, N_2 flow rate 1000ml/min).

Concentration (char :KOH (w/w))	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
1:1	49.33	0.15	3.22	194	891	615.80
3:1	61.36	0.18	2.34	165	701	N/A
5:1	65.26	0.19	2.96	160	469	N/A
7:1	69.72	0.20	3.69	138	360	N/A
10:1	69.48	0.21	4.59	126	287	12.59

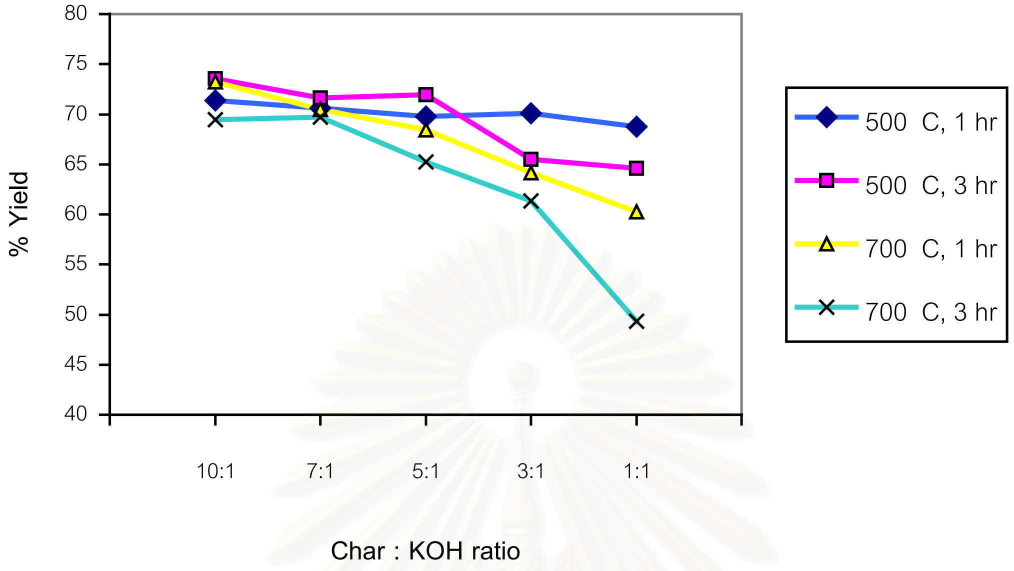

Figure 4.16 Effect of char : potassium hydroxide ratio on % yield at different temperatures and times (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

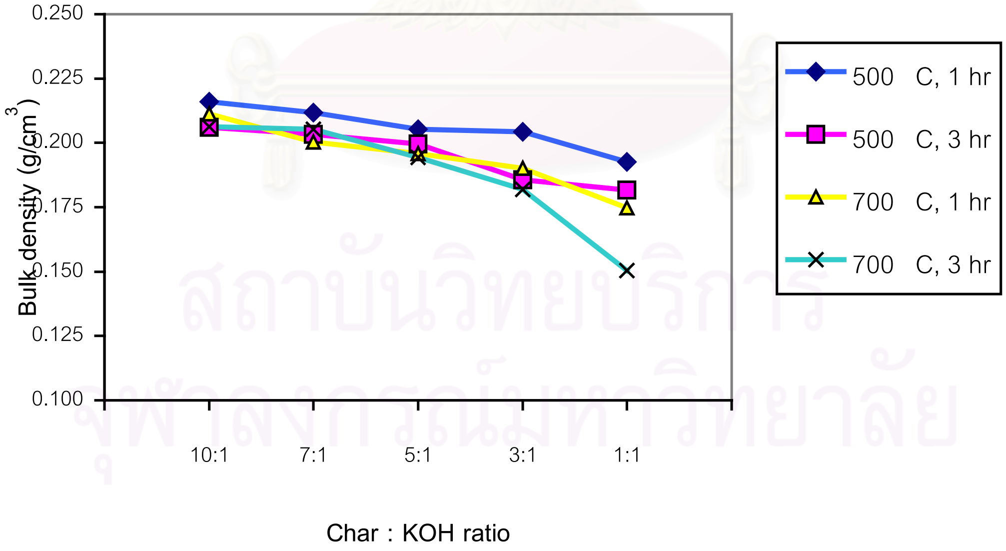

Figure 4.17 Effect of char : potassium hydroxide ratio on bulk density at different temperatures and times (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

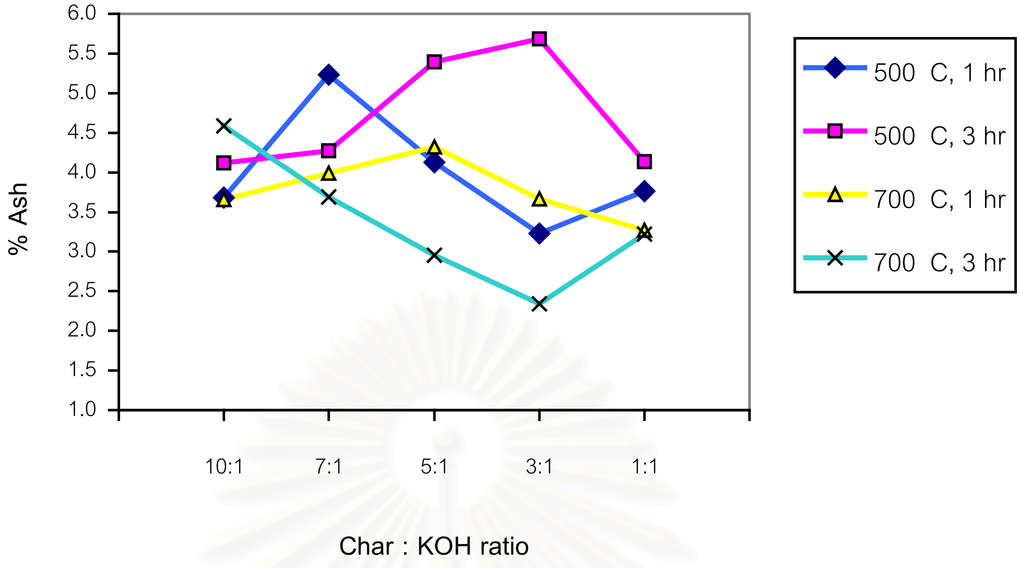

Figure 4.18 Effect of char : potassium hydroxide ratio on % ash at different temperatures and times (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

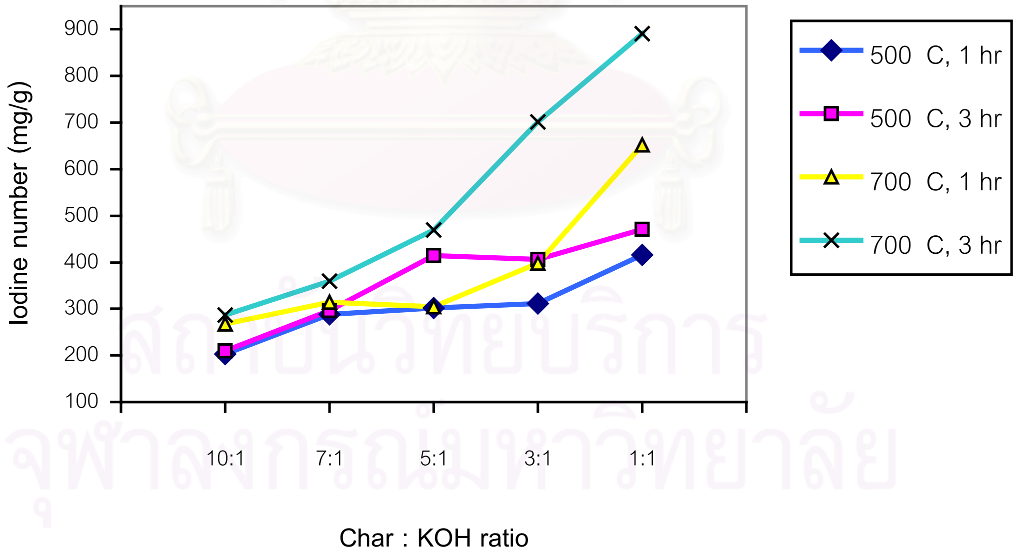

Figure 4.19 Effect of char : potassium hydroxide ratio on iodine number at different temperatures and times (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

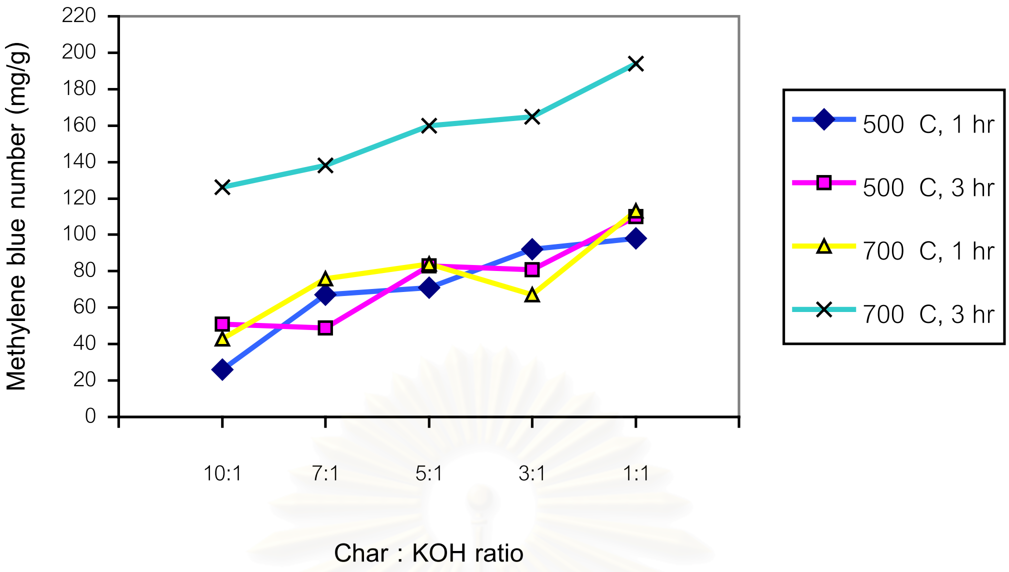

Figure 4.20 Effect of char: potassium hydroxide ratio on methylene blue number at different temperatures and times (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

From **Tables 4.4–4.7** and **Figures 4.16-4.17**, the % yield and bulk density of activated carbon from Para wood decreased conformably when the concentration of potassium hydroxide increased and reached at the minimum of both values at char: KOH ratio 1:1. Potassium hydroxide reacted more with char and volatile matter and diffused quickly out of the surface of particles and substituted –H group by –OK group, so the % yield and bulk density had decreased. However the char : KOH ratio 3:1 to 1:1 for 1 and 3 hr at 500 ^{o}C the % yield and bulk density remained fairly constant. It is probably caused by more potassium hydroxide of higher % concentration of potassium hydroxide inside the particle, which would block volatile matter from gassing out of the surface. From **Tables 4.4 - 4.7** and **Figure 4.18** showed that % ash did not depend upon concentration. It was obvious the temperature that used for activation at 500 and 700 ^{o} C for 1 and 3 hr % ash would be around 2-4 % by weight.

Tables 4.4 – 4.7 and **Figures 4.17 - 4.20**, showed that the iodine number, methylene blue number and B.E.T. surface area would increase when the concentration of potassium hydroxide solution increased. They reached the maximum at char: KOH 1:1. It confirmed that the more reaction took place, the more porosity developed as the result; %

yield and bulk density decreased while iodine number, methylene blue number and B.E.T. surface area increased.

The optimum concentration was 1:1 char : KOH ratios at 700 °C for 3 hr because in this condition has highest iodine number of 891 mg/g, methylene blue number of 194 mg/g and B.E.T. surface area 615.80 m^2/g.

4.2.2.2 The effect of temperature for activation

9 g of 1.18 – 2.36 mm of Para wood char were soaked in 1:1 char: KOH ratio and then were dried. These samples were used for each batch. The nitrogen gas was then allowed to flow through the tube reactor. The stainless tube reactor was heated until the temperature in the tube reactor was raised and fixed at the final temperature 500, 600 and 700 °C. The nitrogen gas was continued, passing through the tube rector for 3 hr. The results of these experiments are shown in **Tables 4.8-4.9** and **Figures 4.21-4.25**.

Table 4.8 Effect of temperature (1:1, 1 hr, N_2 flow rate 1000 ml/min).

Temperature (°C)	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
500	68.76	0.19	3.76	98	416	85.54
600	65.43	0.19	4.33	103	523	N/A
700	60.26	0.17	3.27	113	652	546.41

Table 4.9 Effect of temperature (1:1, 3 hr, N_2 flow rate 1000 ml/min).

Temperature (°C)	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
500	64.62	0.18	4.14	129	471	N/A
600	60.13	0.17	6.23	164	635	N/A
700	49.33	0.15	3.22	194	891	615.80

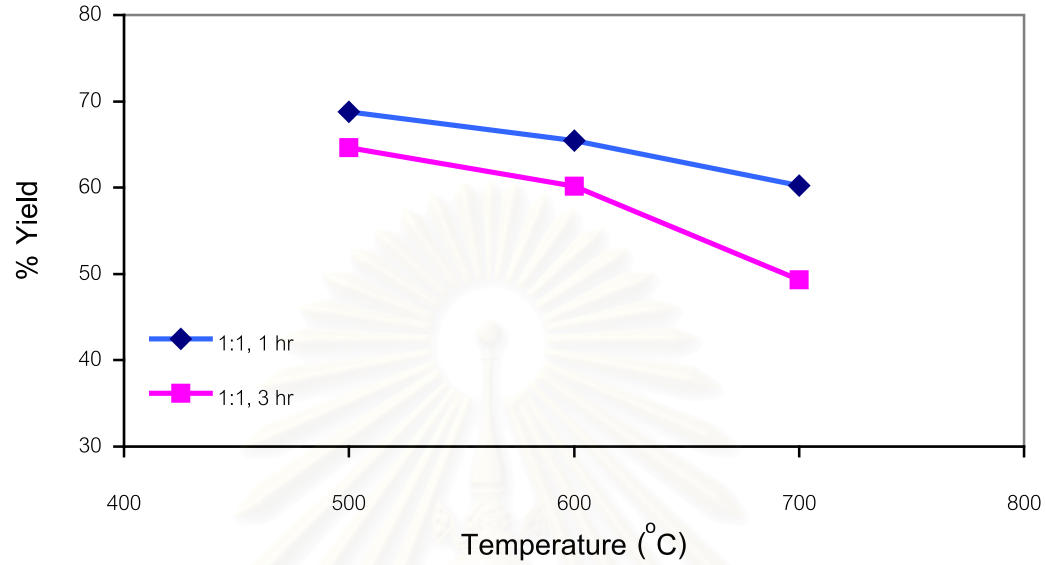

Figure 4.21 Effect of activation temperature on % yield at different times and char : KOH ratio (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

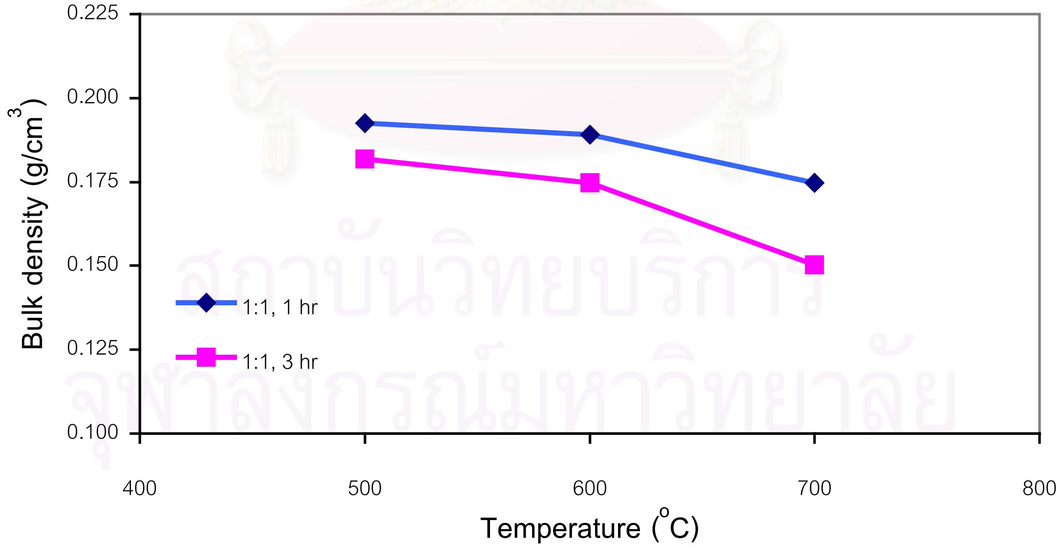

Figure 4.22 Effect of activation temperature on bulk density (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

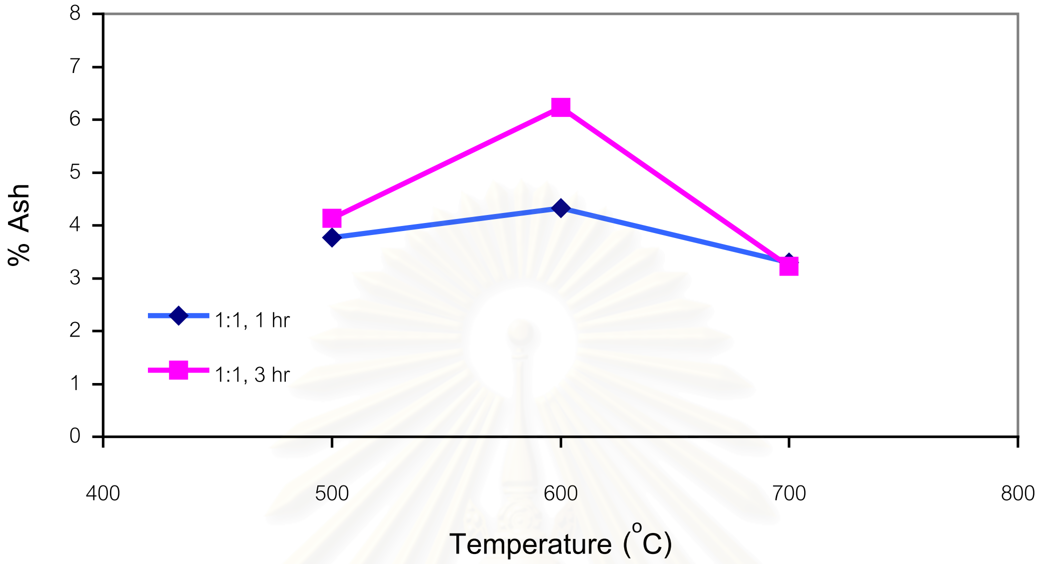

Figure 4.23 Effect of activation temperature on % ash (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

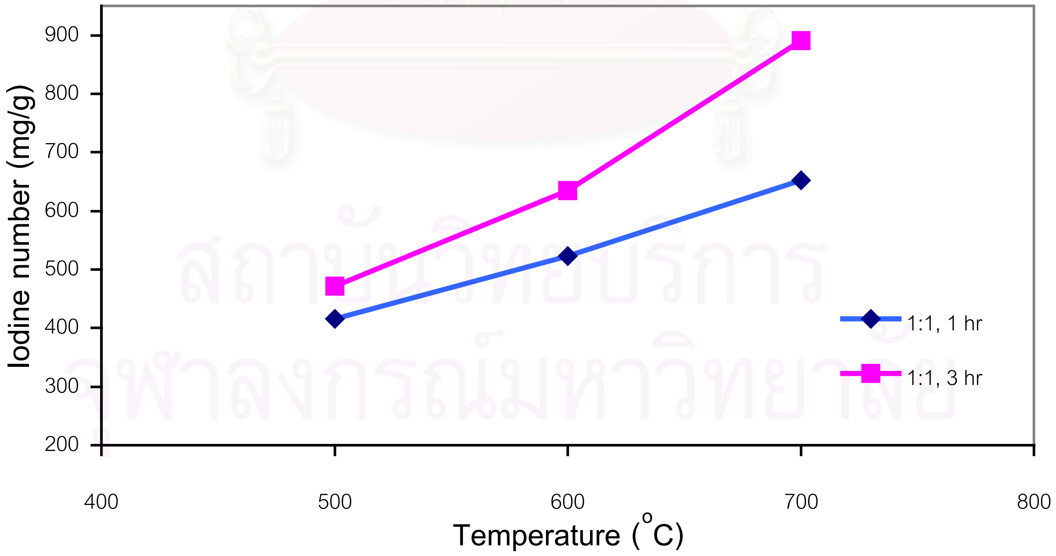

Figure 4.24 Effect of activation temperature on iodine number (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

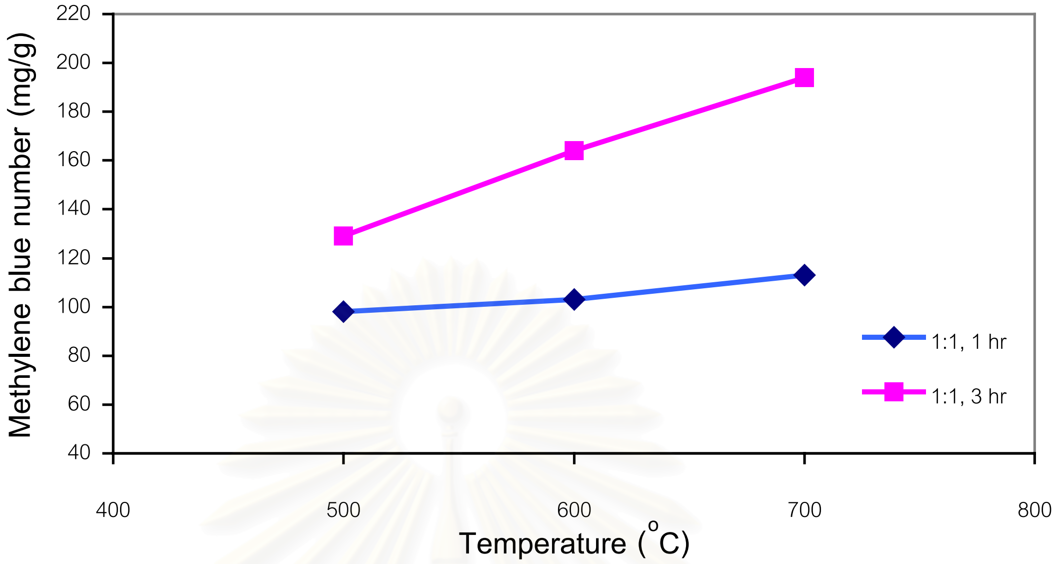

Figure 4.25 Effect of activation temperature on methylene blue number (size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

From **Tables 4.8 – 4.9**, **Figures 4.21 - 4.22**, the % yield and the bulk density of activated carbon from Para wood decrease conformably as activation temperature increased. Comparing between range of 500 to 600 °C and 600 to 700 °C, the range of 500 to 600 °C has slower changing. Because at high temperature, loss of volatile matter was greater than that at low temperature. The increasing of temperature leads to the increasing of porosity development, as a result, the weight of activated carbon decreased. Moreover, the % yield and the bulk density also decreased. The change in the % yield of Para wood was about 5% from 500 to 600 °C, 10.8% from 600 to 700 °C and bulk density from Para wood decreased totally 17.3 % as shown in **Tables 4.8 - 4.9.**

Tables 4.8 - 4.9 and **Figures 4.24 - 4.25**, showed that when the activation temperature increased from 500 to 700 °C, the iodine number increased sharply and had a trend to be at the highest at 700 °C for Para wood. While the methylene blue number increased slightly. The B.E.T. surface area increased as the iodine number, because tar like matter and potassium hydroxide deposited in pores were removed or volatilized well by nitrogen gas from 600 to 700 °C, which generated porosity. The higher activation temperature, the more removal potassium hydroxide results, therefore the iodine number and the methylene blue number increased quickly (see slope in **Figures 4.24** and **4.25**). The % change of iodine number was about 47.13 % from 500 to 700 °C, 33.5 % methylene blue number and B.E.T. surface area were shown in **Tables 4.8-4.9**.

The optimum temperature was 700 °C 1:1 char: KOH ratios for 3 hr because in this condition have highest iodine number of 891 mg/g, methylene blue number of 194 mg/g and B.E.T. surface area 615.80 m^2/g.

4.2.2.3 The effect of time for activation

Para wood char 1.18 – 2.36 mm of particle size and mass of 9 g was soaked in potassium hydroxide solution at char: KOH 1:1 and then was dried. Soaked char was used for each batch. Then it was treated at 700 °C for 1, 2 and 3 hr as activation time with nitrogen gas by passing through the tube reactor. The results of this experiment were shown in **Table 4.10** and **Figures 4.26 - 4.30**.

Table 4.10 Effect of time (1:1, 700°C, N_2 flow rate 1000 ml/min).

Time (hr)	Y (%)	BD G/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
1	60.26	0.17	3.27	113	652	546.41
2	58.42	0.16	3.51	182	670	N/A
3	49.33	0.15	3.22	194	891	615.80

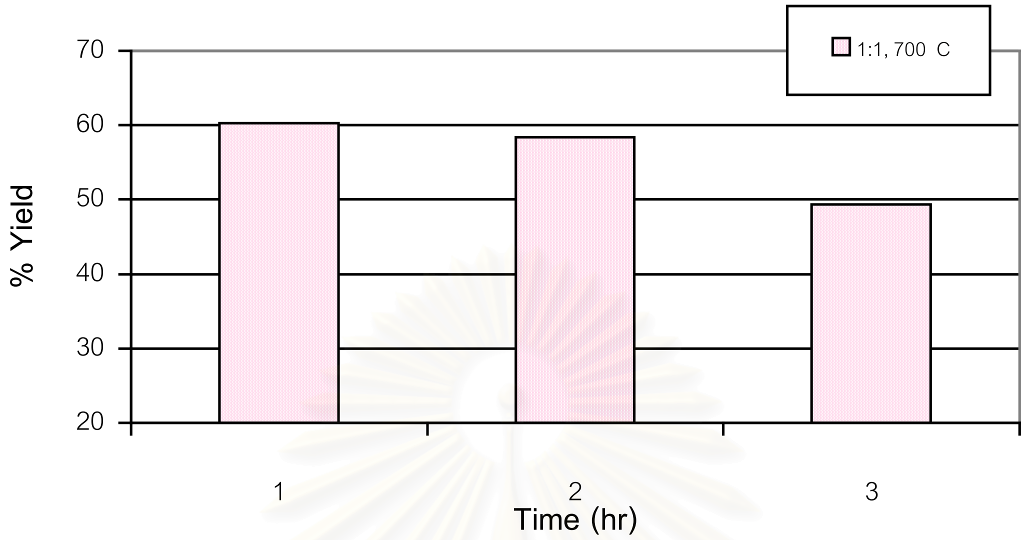

Figure 4.26 Effect of activation time on % yield (char : KOH 1:1, 700 °C, size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

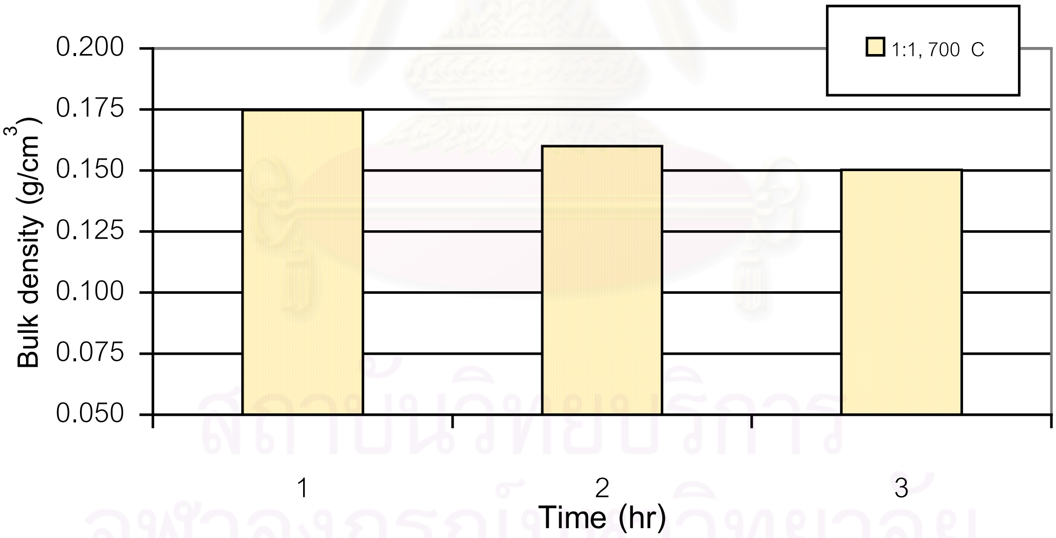

Figure 4.27 Effect of activation time on bulk density (char : KOH 1:1, 700 °C, size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

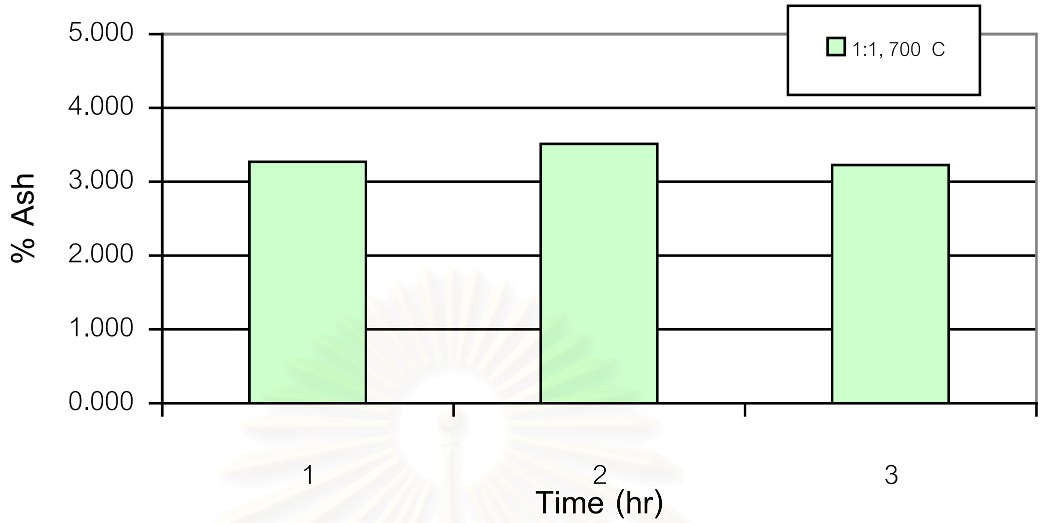

Figure 4.28 Effect of activation time on % ash (char : KOH 1:1, 700 °C, size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

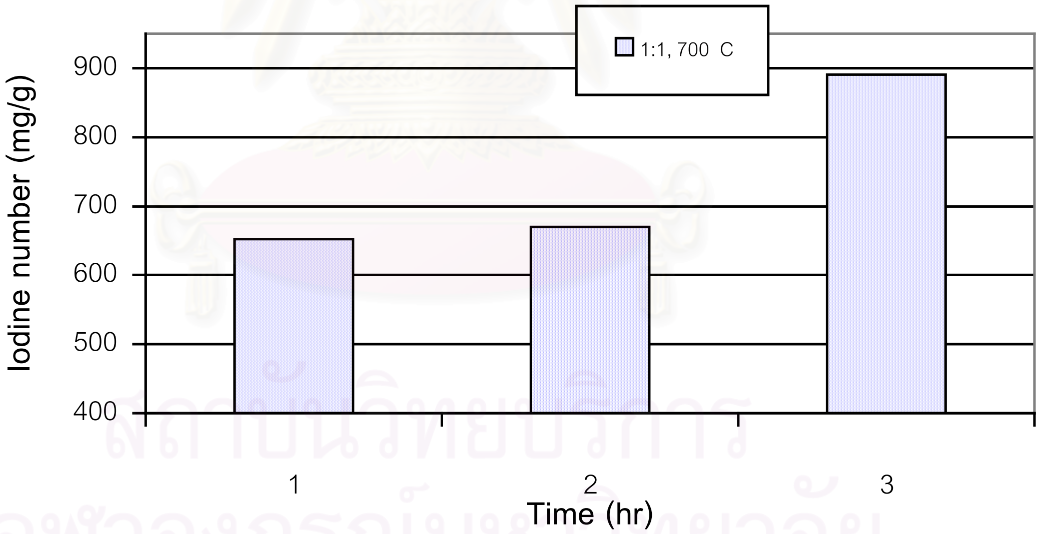

Figure 4.29 Effect of activation time on iodine number (char: KOH 1:1, 700 °C, size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

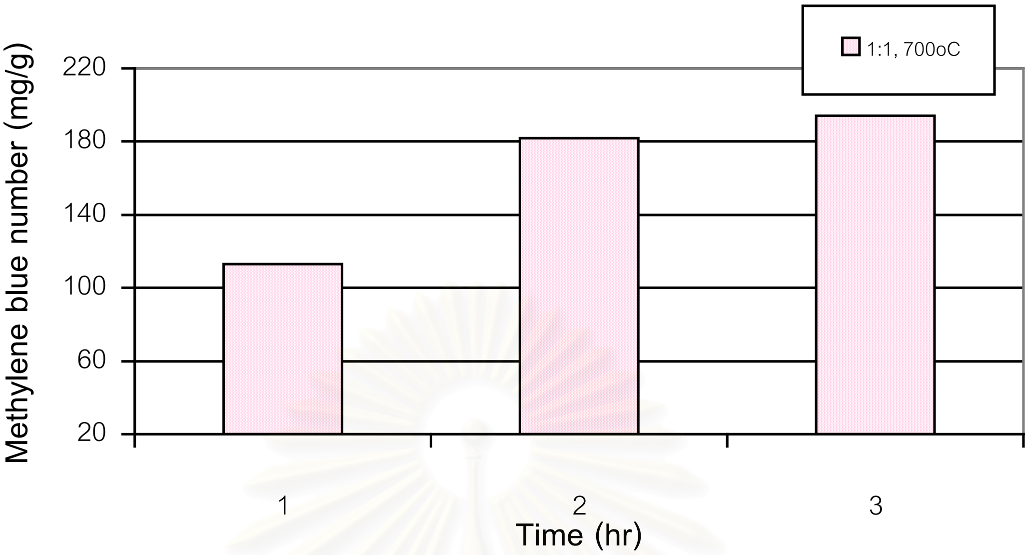

Figure 4.30 Effect of activation time on methylene blue number (char : KOH 1:1, 700 °C, size 1.18-2.36 mm, 9 g, N_2 flow rate1000 ml/min).

Table 4.10 and **Figures 4.29 - 4.30** showed that an increase of activation time could cause an increase of iodine number, methylene blue number and B.E.T. surface area. In the first stage (1-2 hr) iodine number increases slightly but methylene blue number increases sharply, the increasing is caused from volatile matter and moisture in Para wood char. It is evident that at the first stage, it has more mesopores than micropores and when it is left longer time (2 - 3 hr). It is found that iodine number and methylene blue number tend to increase 24.8 % and 6.18 % , respectively. It is because longer activation time (2-3 hr) could make micropores and mesopores increase.

From **Table 4.10** and **Figure 4.26** the % yield of Para wood char decreases slightly and conformably with increasing in the time from 1 to 2 hr (about 3.05 % change), and largely decreased from 2 to 3 hr (15.5 % change). Because the volatile matter outside and inside the particle and char were gasified itself by using potassium hydroxide as catalyst. The gaseous product, volatile matter and potassium hydroxide in majority diffused out of the particle in the beginning time more slowly (see the slope) than longer activation time (from 2 to 3 hr) which less remained volatile matter being deeper in the particle diffused out only. The % bulk density of Para wood char (**Figure 4.27**) decreased in the same trend of the %

yield. These phenomena showed that porosity developed quickly in 3 hr. **Table 4.10** showed the change of % yield and the bulk density.

Table 4.10 and **Figures 4.26-4.30** showed the % ash, iodine number and methylene blue number of activated carbon from Para wood in function of activation time range of 1 to 3 hr. The iodine number, methylene blue number and B.E.T. surface area are increased. In the same trend, the high increasing rate covered in the range of 1 to 3 (from 652 to about 891 mg/g for IA, 113 to about 194 mg/g for MB and to 546.41 to about 615.80 mg^2/g for specific surface area). It could be explained in the same way as % yields that volatile matter and potassium hydroxide diffused out rapidly especially at the external surface, as a result, micropores developed quickly in the form of surface area as well. The % changes of iodine number, methylene blue number and B.E.T. surface area were shown in **Table 4.10.**

The optimum activation time was 3 hr at 1:1 char: KOH ratios 700 °C because in this condition has highest iodine number of 891 mg/g, methylene blue number of 194 mg/g and B.E.T. surface area 615.80 m^2/g.

4.2.2.4 The effect of size of Para wood char for activation

The influence of particle size was determined for different three sizes of Para wood char. They were 0.60-1.18, 1.18-2.36 and 2.36-4.75 mm and soaked in 1:1 char: potassium hydroxide ratio solution. The mass of 9 g of each sample of the Para wood char was carried out at 700 °C while nitrogen gas was passed though the bed for 3 hr. The results of this experiment were shown in **Table 4.11** and **Figures 4.31-4.35**

Table 4.11 Effect of particle Size (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min)

Size (mm)	Y (%)	BD g/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
0.6 - 1.18	48.00	0.148	4.792	202	1069	943.35
1.18 - 2.36	49.33	0.150	3.222	194	891	615.80
2.36 - 4.75	71.51	0.159	2.684	137	446	339.90

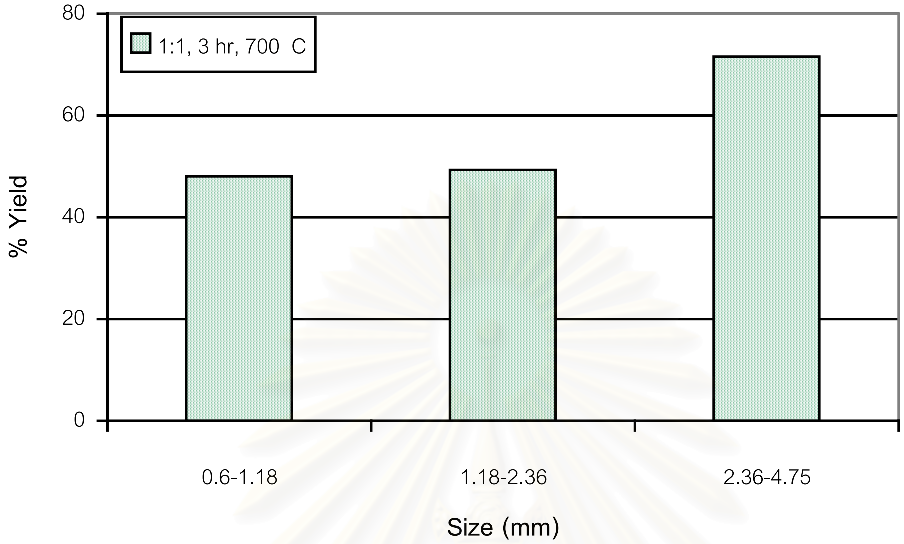

Figure 4.31 Effect of particle size on % yield (char : KOH 1:1, 700 °C, 3 hr, 9 g, N_2 flow rate1000 ml/min).

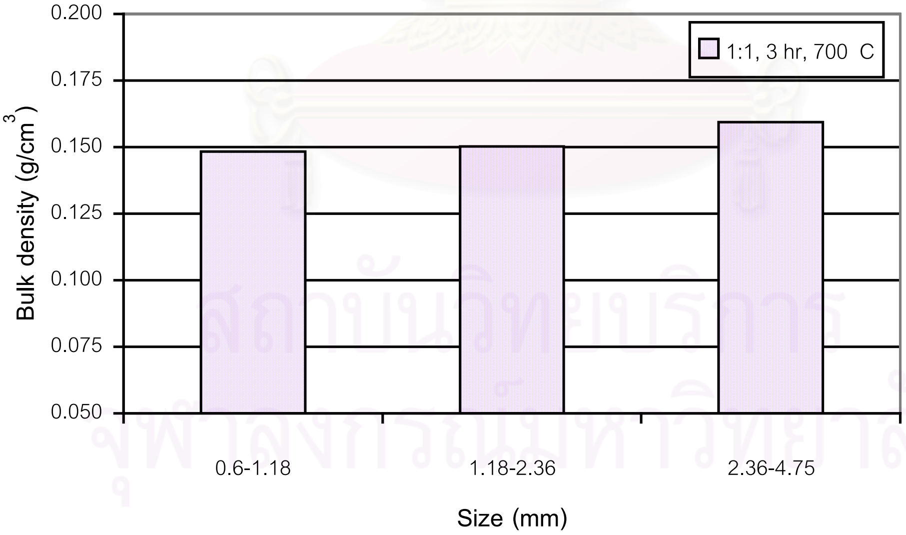

Figure 4.32 Effect of particle size on bulk density (char : KOH 1:1, 700 °C, 3 hr, 9 g, N_2 flow rate1000 ml/min).

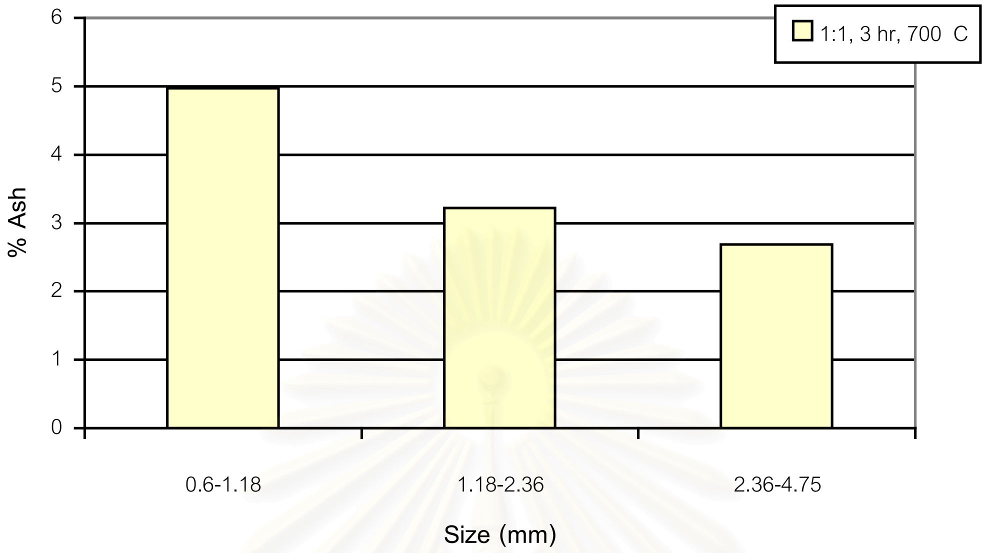

Figure 4.33 Effect of particle size on %ash (char : KOH 1:1, 700 °C, 3 hr, 9 g, N_2 flow rate1000 ml/min).

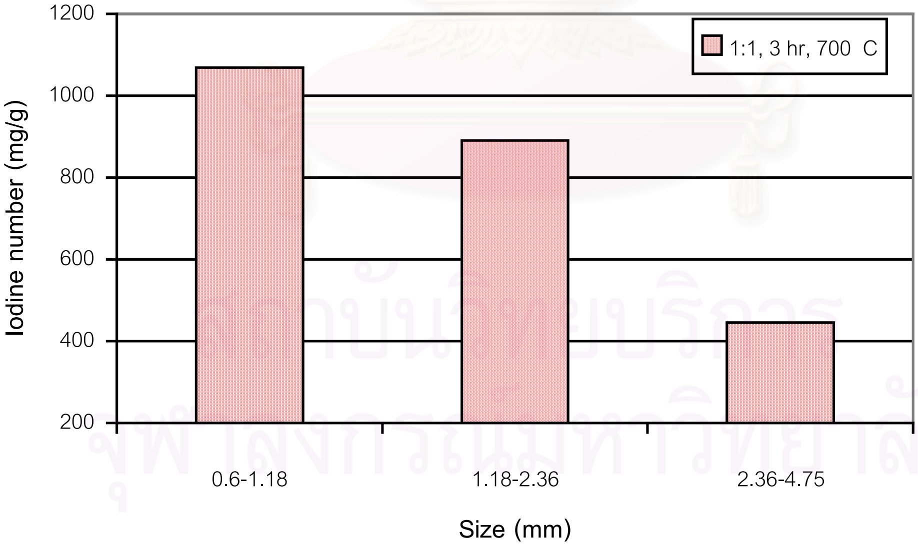

Figure 4.34 Effect of particle size on iodine number (char: KOH 1:1, 700 °C, 3 hr, 9 g, N_2 flow rate1000 ml/min).

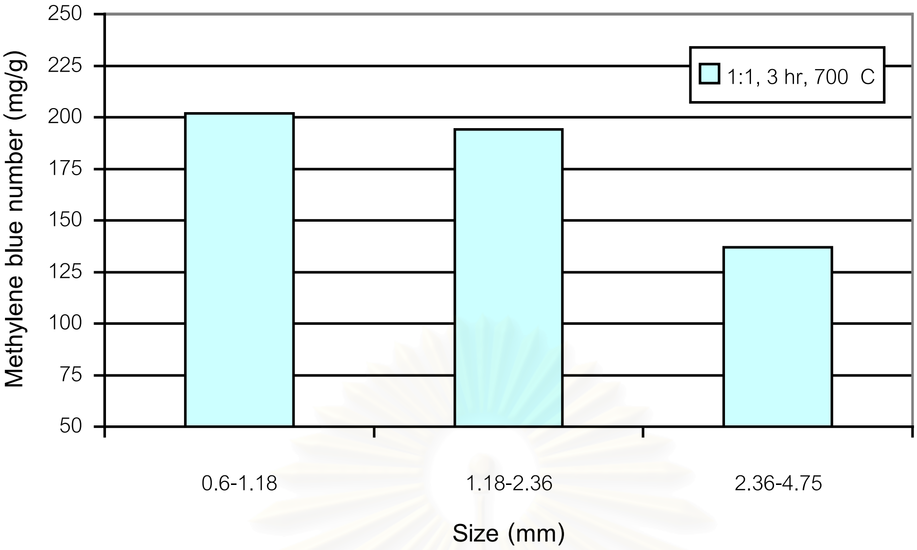

Figure 4.35 Effect of particle size on methylene blue number (char: KOH 1:1, 700 °C, 3 hr, 9 g, N_2 flow rate1000 ml/min).

Table 4.11 and **Figures 4.31 – 4.32** showed the % yield and bulk density. The % yields and bulk density had decreased as the increasing of particle size until both were minimum at 0.60-1.18 mm and went upward again at 2.36-4.75 mm, especially % yield (from 48 to 71.51 %) while bulk density slightly decreased. On the contrary, the iodine number, methylene blue number and B.E.T. surface area **(Figure 4.34)** decreased with increasing of particle size approaching at the maximum at 0.60-1.18 mm and going down at 2.36-4.75 mm, these phenomena could be explained by the physical packing of the bed. When the small particles (range of 0.60-1.18m) were packed in the reactor, it seemed that they packed tightly; as a result, the gaps between particles were narrow, so the volatile and potassium hydroxide were difficult to vaporize out of the fixed bed by flowing nitrogen gas. These caused the high % yield and low development of porosity which conformed high bulk density, low iodine number, methylene blue number and B.E.T. surface area.

The particle size of 0.60-1.18 mm seemed appropriate for flowing of nitrogen gas and caused vary well vaporization of potassium hydroxide and diffusion out of volatile matter from the surface of the particle and the bed, so the characteristic of the activated carbon was the best at this size.

The particle size of 2.36-4.75 mm was bigger about two times than the one of the optimum. They arranged themselves by packing loosely and causing big gaps between particles. The nitrogen gas could flow out rapidly without contact all of the particles or sometimes occurring a channeling was observed; low development of porosity causing higher % yield, bulk density but lower iodine number, methylene number and B.E.T. surface area.

The experimental results showed that the optimum size of Para wood char for activation was 0.60-1.18 mm because the characteristic of activated carbon gave the highest iodine number, methylene number and B.E.T. surface area. Its properties were yield of 48.0 %, bulk density of 0.1482 g/cm^3, iodine number of 1069 mg/g, methylene blue number of 202 mg/g, B.E.T. surface area of 943.35 m^2/g.

4.2.2.5 The effect of alkaline activation

The different reagents as potassium hydroxide and sodium hydroxide were studied to determine the optimum reagent for activation. The mass of 9 g of Para wood char (0.06 - 1.18 mm) were soaked in different reagent at char: reagent ratio 1:1 and then were dried. These samples were used for each batch. The reactor was heated until the temperature in the tube increased and being fixed at the final temperature 700 °C. The nitrogen gas was passing up through the tube reactor for 3 hr. The results of this experiment were shown in **Table 4.12** and **Figures 4.36-4.40.**

Table 4.12 Effect of alkaline (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min and size 0.60-1.18 mm)

Alkaline	Y (%)	BD G/cm^3	Ash (%)	MB (mg/g)	IA (mg/g)	B.E.T. (m^2/g)
KOH	48.00	0.114	5.236	202	1069	943.35
NaOH	55.15	0.148	4.792	146	465	286.48

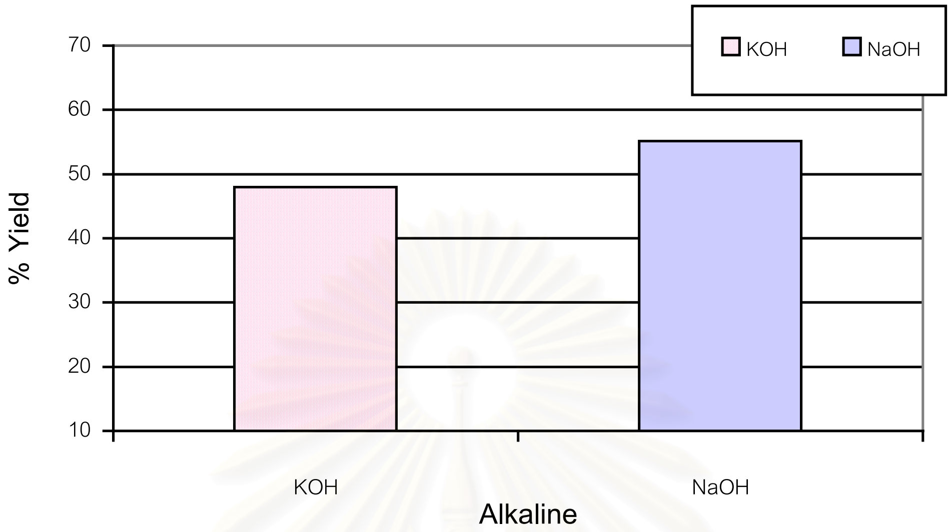

Figure 4.36 Effect of alkaline solutions on % yield (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min and size 0.60-1.18 mm).

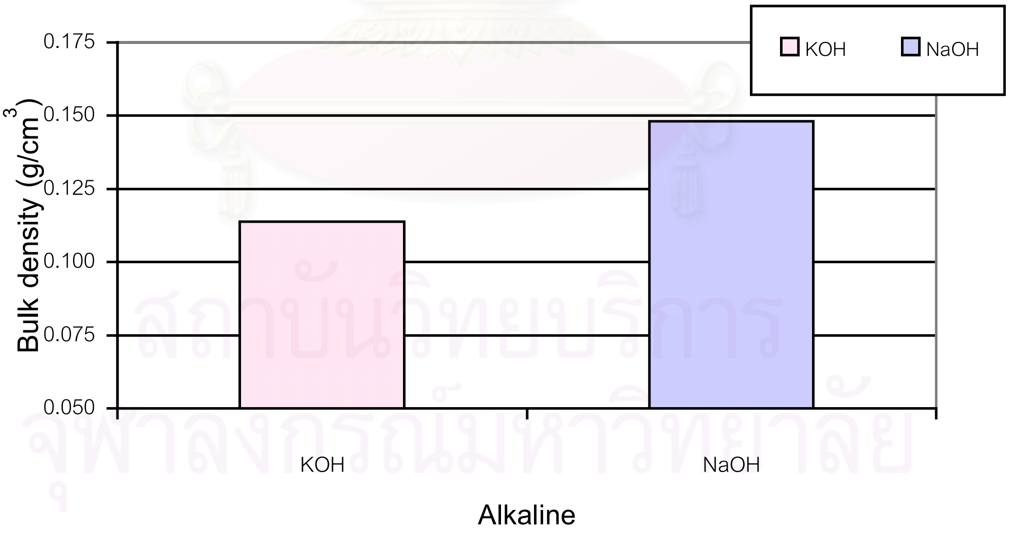

Figure 4.37 Effect of alkaline solutions on bulk density (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min and size 0.60-1.18 mm).

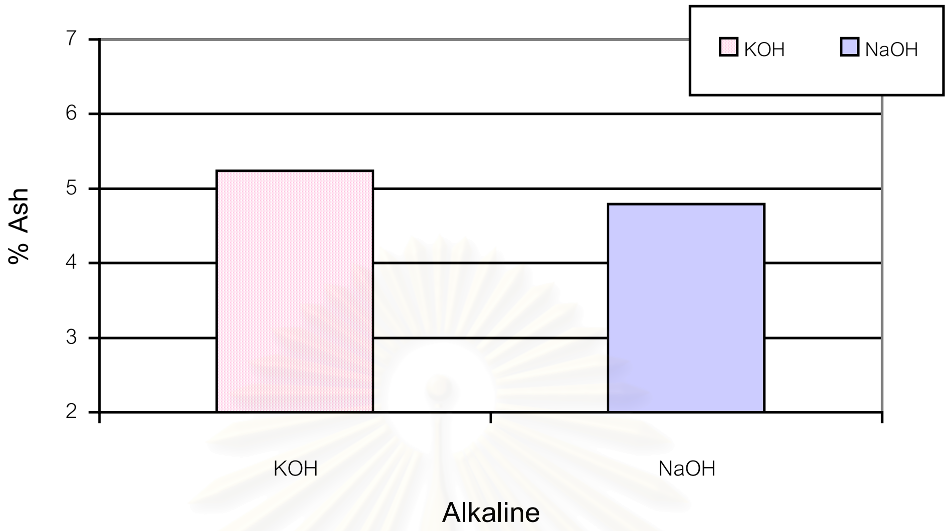

Figure 4.38 Effect of alkaline solutions on % ash (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min and size 0.60-1.18 mm).

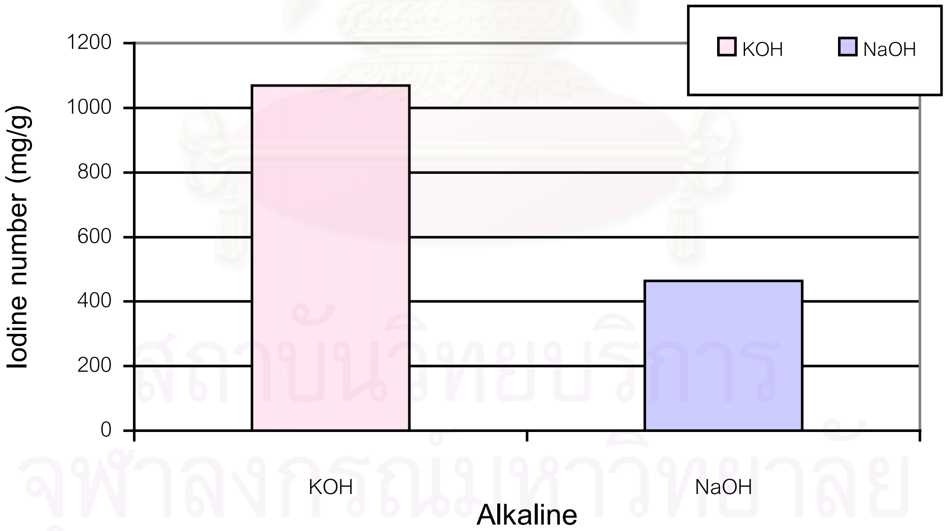

Figure 4.39 Effect of alkaline solutions on iodine number (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min and size 0.60-1.18 mm).

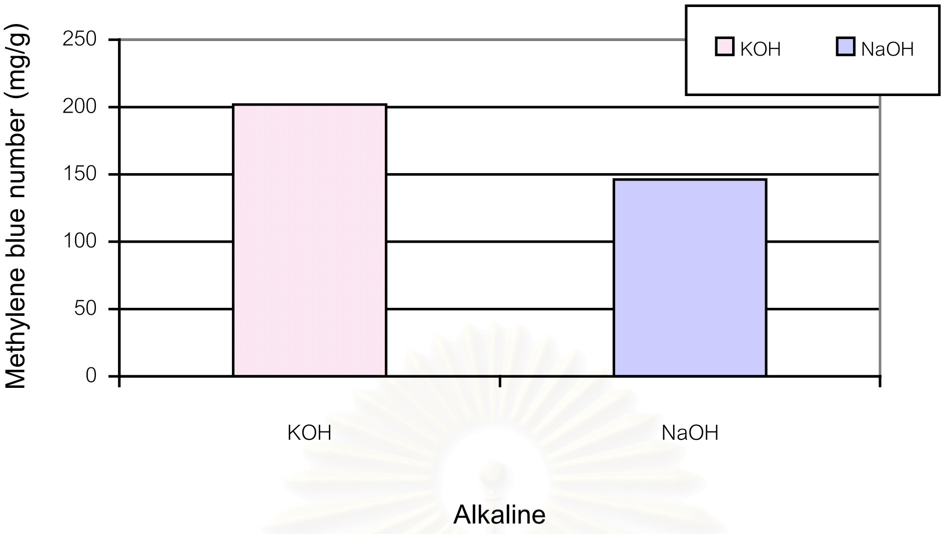

Figure 4.40 Effect of alkaline solutions on methylene blue number (1:1, 3 hr, 700°C, N_2 flow rate 1000 ml/min and size 0.60-1.18 mm).

Table 4.12 and **Figures 4.38-4.40**, showed the iodine number, methylene blue number and B.E.T. surface area which KOH, as activating agent is higher property than NaOH. It is because NaOH is stronger alkaline than KOH. NaOH could react with char more violent and caused larger pores than using KOH.

Figure 4.38, showed that % ash gave a bit which KOH as activating agent higher than NaOH. **Figures 4.36 - 4.37** showed % yield and bulk density, which NaOH as activating agent gave higher value than KOH. It is because NaOH had high reaction inside the char as a result the large-scale pores (macropores) were developed by corresponding to the higher % yield and bulk density. (NaOH caused violent internal reaction, which then resulted large-scale pores. Meanwhile, KOH reacted surface area and then resulted a large number of small-scale pores. Therefore, it was found out that when using NaOH as activating agent, witll give higher % yield and higher bulk density value as shown in **Table 4.12**

The experimental results showed that the optimum reagent for alkaline solution activation was using KOH. Because the characteristic of activated carbon gave the highest iodine number and methylene blue number. Properties were at yielding of 48.00 %, bulk density of 0.114 g/cm^3, 5.24 % ash, iodine number of 1069 mg/g, methylene blue number of 202 mg/g and B.E.T. surface area of 943.35 m^2/g.

Table 4.13 Comparison of chemical activation with physical activation

Description	Physical	Chemical	
		By KOH	By NaOH
Raw material	Para wood	Para wood	Para wood
Carbonization	400 °C 45 min.	400 °C 45 min	400 °C 45 min
Activation	800 °C 2 hr	700 °C 3 hr	700 °C 3 hr
Activating agent	CO_2 + Steam	KOH	NaOH
Size	0.60 - 1.18 mm	0.60 – 1.18 mm	0.60 – 1.18 mm
% yield	44.44 %	48 %	55.15 %
Iodine number	512 mg/g	1069 mg/g	465 mg/g
Methylene blue number	154 mg/g	202 mg/g	146 mg/g
BET surface area	-	943.35 m^2/g	286.48 m^2/g

Table 4.13 showed the comparison properties of activated carbon obtained by physical and chemical activates. Physical activation gave the same value of Iodine number and methylene blue number as chemical activation by using NaOH (shown as in **Figures 4.42** and **4.44**) whereas KOH gave considerably higher (shown in **Figure 4.43**). In case of using oxidizing gases, it seemed that the gases were too strong oxidizing for the soft material as Para char wood, which normally, has lots of cavities inside. Meanwhile as strong alkaline, NaOH caused high reaction inside the char, as a result, the larger pore size appeared. Then char was developed which corresponded to the lower Iodine number (shown in Figure **4.41**). In case of using KOH, it seemed appropriate for char wood activation, it gave the high Iodine number which corresponds the high B.E.T. surface area. Finally, properties of activated carbon prepared from KOH activation was used as high commercial grade.

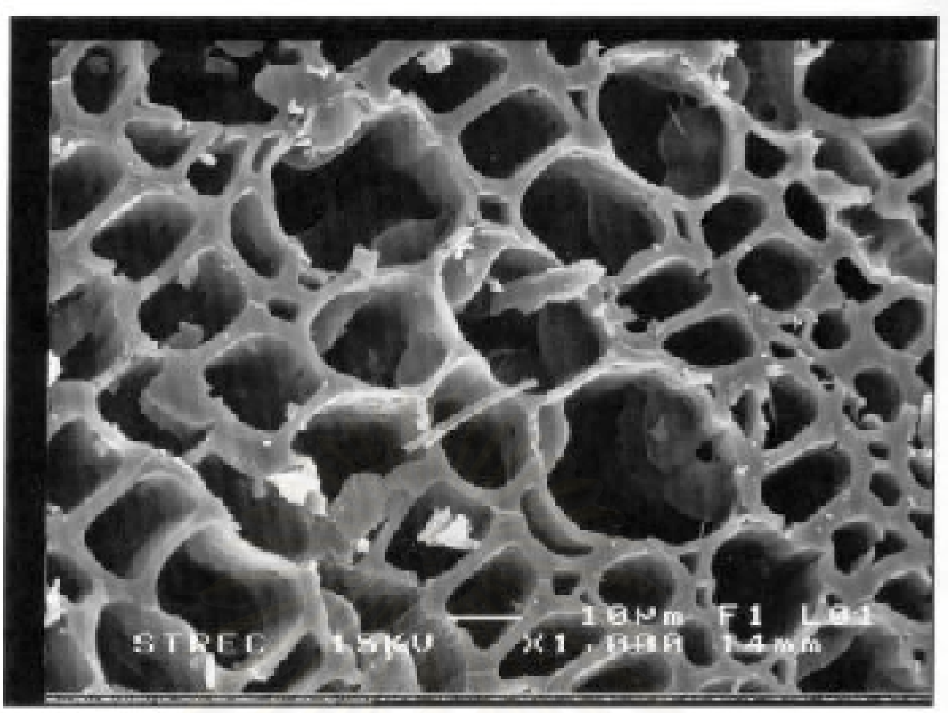

Figure 4.41 SEM microgarph of carbonized Para wood char at 400 °C for 45 min.

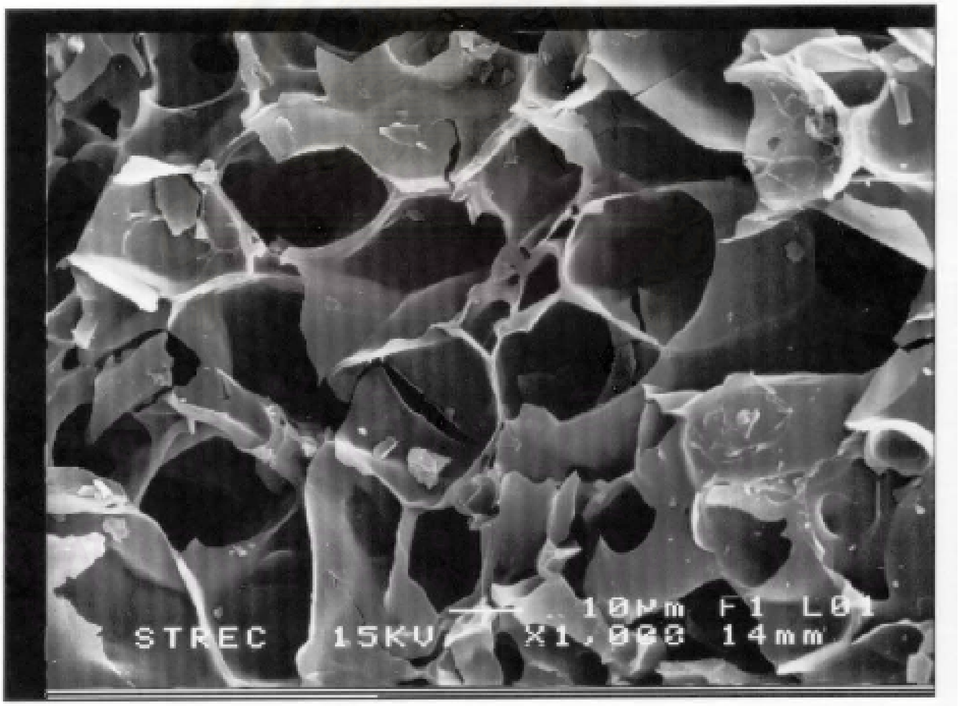

Figure 4.42 SEM micrograph of activated carbon from para wood activation by oxidizing gas (at 800 °C, 3 hr.for activation time,1.18 – 2.36 mm, fixed flow of CO_2 500 ml/min, H_2O 10 g/min and air 5 ml/min).

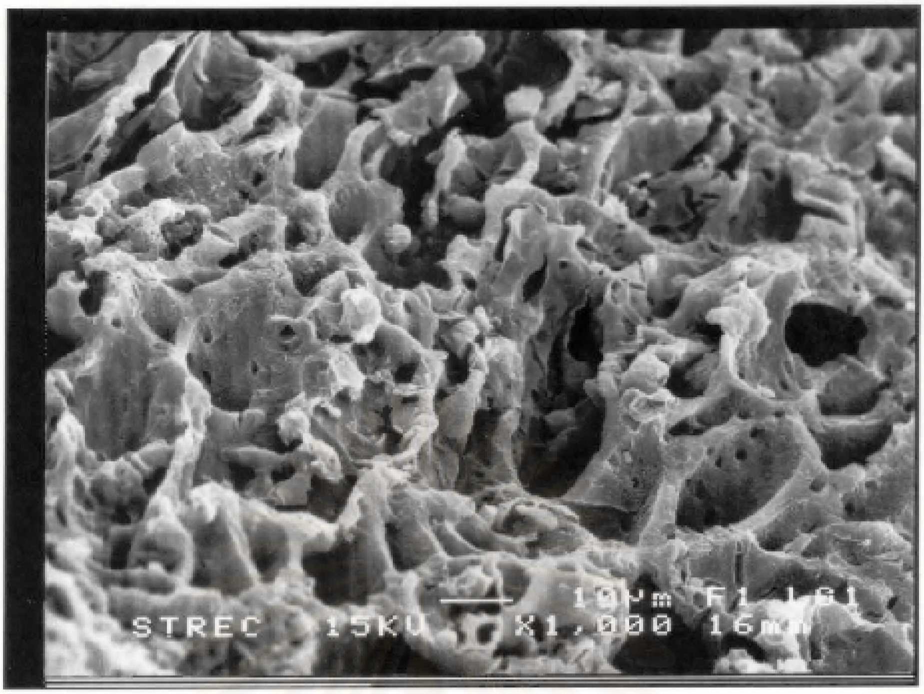

Figure 4.43 SEM micrograph of activated carbon from para wood activation by KOH (at 700 °C, 3 hr for activation time, 0.60 – 1.18 mm, char: KOH ratio = 1:1).

Figure 4.44 SEM micrograph of activated carbon from para wood activated by NaOH (at 700 °C, 3 hr for activation time, 0.60 – 1.18 mm, char: NaOH ratio 1:1).

4.3 Comparison of this work with other works

The comparison of this work with other works was divided into three cases; the first compared with Nitcharee Ninlanon's (1997) in case of using wood as raw material and using CO_2 and superheated steam as oxidizing agent, the second compared with Thawatchai Tuncharoensap's (2001) in case of using KOH as activating agent but different raw material, and last compared with D. Lozano-Castallo et. al.'s, in case of using NaOH as activating agent but different raw material, the characteristics of activated carbon obtained were expressed in **Tables 4.13 - 4.15**, respectively.

Table 4.14 Comparison of this work with Nitcharee Ninlanon's (similar raw material but different activation procedure)

Description	This work	Nitcharee's
Raw material	Para wood	Mangrove wood
Carbonization	400 °C 45 min.	300 °C 60 min
Activation	800 °C 3 hr.	850 °C 1 hr
Activating agent	CO_2 500 ml/min and steam 10 ml/min	CO_2 5 ml/min and Steam excess
Size	0.60 - 1.18 mm	0.60 - 1.18 mm
% yield	44.44 %	27.47 %
Iodine number	512 mg/g	675 mg/g
Methylene blue number	154 mg/g	254.73 mg/g
B.E.T. surface area	N/A	639.74 m^2/g

Nithcharee produced the activated carbon from Mangrove wood by 2 steps: carbonization and activation by using superheated steam (excess) and carbon dioxide. The optimum condition for activation was at 850 °C for 1 hr. and reported by B.E.T. surface area of 639.74 m^2/g, iodine number of 675.14 mg/g and methylene blue number 254.73 mg/g.. In this work with similar raw material, the iodine number of 512 mg/g and methylene blue number of 154 mg/g are obtained 800 °C for 3 hr. From **Table 4.14** when comparing absorption iodine and methylene blue of this work with Nitcharee's, it was found that Nitcharee's result was higher. This is probably, because flow rate of activating agent is different. It is obvious that this work used CO_2 which flow rate is higher than that of Nitcharee. Meanwhile, Nitcharee used excess steam. It could be concluded that steam effected porosity development more than CO_2. But since CO_2 is cheaper in industry, this work, therefore, used CO_2 for the benefit of production for industrial sector in the future.

Table 4.15 Comparison of this work with Thawatchai Tuncheroensap's (2001) (different raw material but same activating agent)

Description	This work	Thawatchai's
Raw material	Para wood	Thai lignite
Carbonization	400 °C 45 min.	450 °C 45 min
Activation	700 °C 3 hr.	800 °C 4 hr
Activating agent	KOH	KOH
Char : KOH ratio	1:1	1: 0.7
Size	0.60 - 1.18 mm	0.50 – 0.85 mm
% yield	48.00 %	50.87 %
Iodine number	1069 mg/g	846 mg/g
Methylene blue number	202 mg/g	229 mg/g
B.E.T. surface area	943.35 m^2/g	1292 m^2/g

Thawatchai produced the activated carbon form Thai lignite through chemical activation by using KOH as activating agent .It was found that the optimum condition for activation was at 1: 0.7 of ratio char : reagent temperature at 800 °C for 4 hr. and particle size range 0.50 – 0.85 mm., which the properties of obtained activated carbon was a yield

50.87 %, bulk density 0.318 g/cm^3, 14.61 % ash, 846 mg/g of iodine number, 229 mg/g methylene blue number and 1292 m^2/g B.E.T. surface area. This work produced the activated carbon form Para wood which used the same activating agent, (KOH) .It was found that the optimum condition for activation was at 1:1 of ratio char : reagent temperature at 700 °C for 3 hr. and particle size range 0.60 – 1.18 mm., which the properties of obtained activated carbon was a yield 48 %, 1069 mg/g of iodine number, 202 mg/g methylene blue number and 943.35 m^2/g B.E.T. surface area.

From **Table 4.15** show that when comparing to absorption iodine, it was found that this work gave higher iodine adsorption than that of Thawatchai. However, it appeared that methylene blue number and B.E.T. surface area lower than that of Thawatchai. This is probably because of different scale of porosity. Thawatchai's porosity could be very small scale (supermicropores) which did not allow iodine to insert. Meanwhile, N_2, which used for measuring B.E.T. surface area, has smaller size as shown in **Table 4.15**. Besides, it could be different raw material. From this study, Para wood used in this work has structure with existing porosity of xylem & phloem (**Figure 4.41**). When activated by this work, it would expand the existing porosity or create new porosity in some part (**Figure 4.43**). Meanwhile, Thawatchai's Thai lignite was activated with KOH. The porosity occurred would be new ones rather than expansion of the existing ones.

Table 4.16 Comparison of this work with D. Lozano-Castallo et. al.'s (different raw material but same activating agent)

Description	This work	D. Lozano-Castallo
Raw material	Para wood	Spanish anthracite
Carbonization	400 °C 45 min.	N/A
Activation	700 °C 3 hr.	750 °C 1 hr
Activating agent	NaOH	NaOH
Char : NaOH ratio	1:1	1: 3
Nitrogen flow rate	1000 ml/min	500 ml/min
Size	0.60 - 1.18 mm	< 0.60 mm
% yield	55.15 %	64.00 %
Iodine number	465 mg/g	N/A
Methylene blue number	146 mg/g	N/A
BET surface area	286.48 m^2/g	1248 m^2/g

D. Lozano-Castallo prepared the activated carbon form Spanish anthracite, through chemical activation by using NaOH as activating agent. It was found that the optimum condition for activation was at 1: 3 of ratio char: reagent temperature at 750 °C for 1 hr. and particle size < 0.60 mm., which the properties of obtained activated carbon was a yield 64 % and 1248 m^2/g B.E.T. surface area. This work produced the activated carbon form Para wood which the same activating agent (NaOH). It was found that the optimum condition for activation was at 1:1 of ratio reagent: char temperature at 700 °C for 3 hr. and particle size range 0.60 – 1.18 mm..The properties of obtained activated carbon was a yield, 55.15 %, 465 mg/g of iodine number, 146 mg/g methylene blue number and 286.48 m^2/g B.E.T. surface area.

Table 4.16 shows that when comparing to B.E.T. surface area of this work with D. Lozano-Castallo's, it was found out that B.E.T. surface area of D. Lozano-Castallo was higher. This is because of different raw materials. Anthracite contains high quantity of fixed carbon and higher density than Para wood. When activated with NaOH, it would create new porosity. Meanwhile using Para wood as raw material. In this research, porosity of xylem and phloem already existed. When NaOH was used for activation, it would rather expand the pores than developing new ones.

Besides, it was found that this might effect from ratio of char : NaOH used for activation. This work used ratio char : NaOH 1:1 while D. Lozano-Castallo's used ratio 1:3. It is clear that more than 3 times of NaOH was used in this work. Therefore, it is possible that the higher ratio of NaOH used in activation with anthracite would result in building more porosity.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The experimental results showed the possibility for the production of activated carbon from Para wood. In this research, experiment was undertaken to produce activated carbon from Para wood by production process, which concluded carbonization and activation. The variables studied in carbonization step were temperature (350 – 450 ^{o}C) and carbonized time (45, 60, 90, and 120 minutes). The suitable condition found for carbonization was at temperature 400 ^{o}C for 45 minutes with 27.51 % yield, 70.46% fixed carbon, 25.90 % volatile matter and 2.31 % ash.

The activation step was divided into two methods; physical activation by oxidizing gas and chemical activation by alkaline solution (potassium hydroxide and sodium hydroxide). Studied variables in this research were activation temperature, activation time and size of Para wood char including ratio of char: alkaline. From the results of the experiment, it was found that the suitable condition for physical activation was 800 ^{o}C in 3 hours using char from Para wood sized 0.60-1.18 mm. Activated carbon obtained was a yield 44.44%, 0.21 g/cm^{3} bulk density, 7.33 % ash, iodine number 512 mg/g and methylene blue number 154 mg/g. Whereas the suitable condition for chemical activation both using KOH and NaOH as activating agent 700 ^{o}C for 3 hours using char from Para wood size 0.60 – 1.18 m. Char activated obtained from activation by using KOH as activating agent has 48.00 % yield, 0.114 g/cm^{3} bulk density, 5.24 % ash, iodine number 1069 mg/g, methylene blue number 202 mg/g and BET surface are 943.35 m^{2}/g. Meanwhile activated char from using NaOH as activating agent would produce yield 55.15%. bulk density 0.148 g/cm^{3} , ash 4.79 %, iodine number 465 mg/g , methylene blue number 146 mg/g and B.E.T. surface number 146 mg/g and B.E.T. surface area 286.48 m^2/g. Finally, the properties of activated carbon prepared from KOH activation was used as high commercial grade.

5.2 Future works

1. Experiment studied by using KOH or NaOH as an activating agent in fluidized bed.
2. Experiment studied by using KOH or NaOH and oxidizing gas (steam and CO_2) as an activating agent.

REFERENCES

1. Boonkri S., Mechanical properties of rubber wood composites containing poly (styrene-co-acrylonitril) and poly(methylmethacrylate-co-acrylonitrile). Master's Thesis, Program of Petrochemistry and Polymer science, Faculty of Science, Chulalongkorn University, 2000.
2. Karuna Wiwattanakantang. An economic analysis of Thai oil palm supplies response. Master's Thesis, Faculty of Economic, Thammasat University, 1994.
3. Oil palm industry. Thailand Business (April 1986): 62-64.
4. Irving et. al. S.Chemical Engineering *43* (February 1990).:
5. Gerhartz, H., Yamamoto, Y.S., and Campbell, F.T. Activated carbon. Ullmann's Encyclopedia of Industrial Chemistry. *A5*(1986): 124-140.
6. Allport, H.B. Activated carbon. Encyclopedia of Science & Technology. *7*,1992.: 174-178.
7. Patrick, J.W. Porosity in Carbons: Characterization and Applications. Carbon Research Group, Department of Chemical Engineering, University of Technology Loughborough Leicestershire, UK, 1995.
8. Hassler, J.W. Purification with Activated Carbon. New York: Mercel Dekker, 1974.
9. Bansal, R.C., Donnet, J.B., and Stoeckil, F. Active Carbon. New York: Mercel Dekker, 1988.
10. Jankowska, H., Swiatkowski, A., and Choma, Active Carbon. Warsaw: Ellis Horwood, 1991.
11. Kiselev, A.V. Journal of Colloid Interface Science *28*, 1968.: 265-271.
12. Arriagada, R., Gercia, R., and Reyes, P. Steam and carbon dioxide activation of *Eucalyptus globulus* charcoal. J. Chem. Tech. Biotechnol. *60* (1994): 427-345.
13. Tancredi, N., Cordero, T., Mirasol, J.R., and Rodriguez, J.J., Activated carbons from Uruguayan eucalyptus wood. Fuel 75, No. 15 (1996): 1701-1706.
14. Zhonghua Hu, Preparation high surface area activated carbon from coconut shell by chemical activation, Carbon, No. 63 (2000) : 173-181.

15. Ninlanon N. Production of activated carbon from Mangrove wood. Master's Thesis, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, 1994.

16. D. Lozano-Castallo. Preparation activated carbon form Spanish anthracite by KOH activation. Carbon, 67, 2000: 274-280,

17. D. Lozano-Castallo. Preparation activated carbon form Spanish anthracite by NaOH activation. Carbon, 68, 2000: 342-354.

18. Tuncharoensap T. Comparison Properties of Activated Carbon Prepared from Lignite by Chemical and Physical Activation. Master's Thesis, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, 2001.

18. Gregg, S.J., Sing, K.S.W. Adsorption, Surface Area and Porosity. London: Academic Press, 1982.

19. Gergova, K.M., Petrov, N.V., and Minkova, V.N. A comparison of adsorption characteristics of various activated carbons. J. Chem. Tech. Biotechnol. *56* (1993): 77-82.

20. Budinova, T.K., Gergova, K.M., Petrov, N.V., and Minkova, V.N. Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials. J. Chem. Tech. Biotechnol. *60* (1995): 177-182.

21. Panyawatanakit P. Production of activated carbon from palm oil shell: activated by superheated steam. Master's Thesis, Department of Appropriate Technology of resource, Graduate School, Mahidol University, 1997.

22. Thakunmahachai B. Production of activated carbon from palmyra palm shell in fluidized bed. Master's Thesis, Department of Chemical Technology, Faculty of Science, Chulalongkorn Univarsity, 1994.

23. Gergova, K., Eser, S., Schobert, H.H., Klimkiewicz, M., and Brown, P.W. Environmental scanning electron microscopy of activated carbon production from anthracite by one-step pyrolysis-activation. Fuel *74*, No.7 (1995): 1042-1048.

24. Hussein, M.Z., Zainal, Z., Ibrahim, R., Kheong, K.K., and Muhammad, B. The preparation of activated carbons from chips of oil palm trunk catalyzed

by $ZnCl_2/CO_2$: Surface area and porosity studies. J. Chem. Tech. Biotechnol. *64* (1995): 35-40.

25. Tancredi, N., Cordero, T., Mirasol, J.R., and Rodriguez, J.J. Activated carbons from Uruguayan eucalyptus woods. Fuel 75, No. 15 (1996): 1701-1706.
26. Philip, C.A., and Giegis, B.S. Adsorption characteristics of microporous carbons from apricot stone activated by phosphoric acid. J. Chem. Tech. Biotechnol. *67* (1996): 248-254.
27. Sai, P.M., Ahmed, J., and Krishnaiah, K. Production of activated carbon from coconut shell char in a fluidized bed reactor. Ind.Eng.Chem.Res. *36* (1997): 3625-3630.
28. Suravattanasaku T. Production of activated carbon from palm-oil shell by pyrolysis and steam activation in a fixed bed reactor. Master's Thesis, Department of Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University, 1998.
29. Lortong T. Production of activated carbon from used by superheated steam and carbon dioxide activation in a fixed bed reactor. Master's Thesis, Department of Petrochemical and Polymer Science, Faculty of Science, Chulalongkorn University, 1998.
30. Nithechan Ch. Large scales production of activated carbon from peat by carbonization and steam activation in fluidized bed. Master's Thesis, Department of Chemical Technology, Graduate school, Chulalongkorn University,1994
31. Thailand Industrial Standard Institute, Industrial Ministry. Activated carbon. Standard of Commercial Activated Carbon TIS 900-1989: 1-10.
32. American Standard of Testing Material. Standard practice for proximate analysis of coal and coke. Annual book of ASTM standards D 3172-89: 288.
33. American Standard of Testing Material. Standard test method for moisture in the analysis sample of coal and coke. Annual book of ASTM standard D 3173-87: 289-290.

34. American Standard of Testing Material. Standard test method for ash in the analysis sample of coal and coke from coal. Annual book of ASTM standard D 3174-93: 291-294.

35. American Standard of Testing Material. Standard test method for volatile matter in the analysis sample of coal and coke. Annual book of ASTM standard D 3175-89a (Reapproved 1993): 295-297.

36. American Standard of Testing Material. Standard test method for determination of iodine number of activated carbon. Annual book of ASTM standard D 4607-94: 542-545.

37. Japanese Standard Association. Standard testing method of methylene blue number of activated carbon. Japanese industrial standard test method for activated carbon. JIS K 1470-1991.

38. American Standard of Testing Material. Standard test method for apparent density of activated carbon. Annual book of ASTM standard D 2284-89 (Reapproved 1993): 491-493.

39. American Standard of Testing Material. Standard test method for carbon black-surface area by multipoint B.E.T. nitrogen adsorption. Annual book fo ASTM standard D 4820-96a: 756-762.

40. American Standard of Testing Material. Standard test method for chemical analysis of wood charcoal. Annual book of ASTM standard D 1762-84 (Reapproved 1995): 281-282.

Appendices

Appendix A

Table A.1 Properties of commercial activated carbons (TIS 900-1989).

Table A.2 Properties of commercial powdered activated carbon.

Table A.3 Properties of commercial granular activated carbon.

Table A.1 Properties of commercial activated carbons limit by TIS 900-1989

Types	Size	% Moisture	BD (cm^3/g)	IA (mg)
Powdered activated carbon	<150 μm	-	0.20-0.75	>600
Granular activated carbon	>150 μm	<8	>0.36	>600

Table A.2 Properties of commercial powdered activated carbon

Trade names	Raw material	Ash (%)	BD (g/cm^3)	S_{BET} (m^2/g)	MB (mg/g)	LA (mg/g)
UDP CHEMICAL (Thailand)						
MDP 1-7325	Coconut shell	3	0.40-0.55	1200-1300	230	1050
PN3	-	8	0.46	-	-	800
Taiko PKW	Sawdust	2	-	-	-	-
Shirasagi KW	Sawdust	3	-	-	-	-
Nuchar SA	-	3-5	0.37-0.40	-	-	900
Nuchar SN	-	3-5	0.37-0.40	-	-	900
PITTSBURGH ACTIVATED CARBONS						
RB	Bituminous	23	-	1250-1400	-	1200
RC	Bituminous	21	-	1100-1300	-	1100
BL	Bituminous	8.5	-	1000-1100	300	1000
C	Bituminous	14	-	1000-1100	-	900
GW	Bituminous	12	-	1000-1100	180	700

able A.3 Properties of commercial granular activated carbon.

Trade names	Raw material	Ash (%)	BD (g/cm^3)	S_{BET} (mg/g)	MB (mg/g)	IA (mg/g)
UDP CHEMICAL (Thailand)						
MD-G 7746	Coconut shell	3	0.40-0.45	1100-1200	200	1050
MD-W 7830	Coconut shell	3	0.50-0.55	1150-1250	220	1050
SUTCLIFFE SPEAKMAN (England)						
	Coal	6-16	0.40-0.56	600-1250	-	-
	Coconut shell	1-4	0.40-0.59	700-1500	-	-
NORIT ACTIVATED CARBON						
PK1-3	Peat	6	-	800	-	800
Nuchar 681	Bituminous	-	0.43-0.46	1100	-	-
AG-5	-	6	0.38-0.45	900-1100	-	-
PJAC(Japan)						
CG-4X10	Coconut shell	5	0.42-0.47	1200-1300	170	1050
CG-6X8	Coconut shell	5	0.42-0.47	1200-1300	170	1100
CW-8X30	Coconut shell	5	0.45-0.50	1050-1150	170	1050
SYBRON	Bituminous	-	0.50-0.55	900	220	900
IONAC P-50(USA)						
Calgon	Bituminous	-	-	850-900	-	850
Filtrasorb						
100-200	Bituminous	10	0.48	950-1050	-	900
CALGON						
SGL						
PITTSBURGH ACTIVATED CARBONS						
Vapor phase						
-PCB	Bituminous	4.0	0.44	-	-	1200
Liquid phase						
-CAL	Bituminous	8.5	0.44	-	-	1000

Appendix B

Appendix B.1 Standard Test Method for Chemical analysis of Wood Charcoal (ASTM D 1762-84).

Appendix B.2 Standard Test Method for Apparent Density of Activated Carbon (ASTM D 2884-89).

Appendix B.3 Standard Test Method for Moisture in activated Carbon (ASMT D 2867-95).

Appendix B.4 Standard Test Method for Total Ash Content of Activated Carbon (ASTM D 2866-94).

Appendix B.5 Standard Test Method for Determination of Iodine Number of Activated Carbon (ASMT D 4607-94).

Appendix B.6 Standard testing method of Methylene blue number of Activated (JIS K 1470-1991).

Appendix B.7 Standard Test Method for Carbon Black-Surface area by multipoint B.E.T. Nitrogen Adsorption (ASTM D 4820-96a).

Appendix B.1

Standard Test Method for Chemical analysis of Wood Charcoal (ASTM D 1762-84)

This test method covers the determination of moisture, volatile matter, and ash in charcoal made from wood. The sample is ground in a specified manner and the moisture determined as loss in a drying oven at 105 °C. Volatile matter is determined as loss in weight at 950 °C under specified conditions. Ash is determined as the residue after burning to constant weight 750 °C.

Procedure (for Activated carbon passing A No. 50 Sieve)

1. Make duplicate determinations.
2. ***Moisture*** Heat the muffle furnace to 750 °C and place previously ignited porcelain crucible (*Note1*) and covers in the furnace for 10 min. Cool the crucibles in a desiccator for 1 hr. Weigh the crucibles and add to each approximately 1 g, weighed to the nearest 0.1 mg, of the ground sample. Place the Samples in the oven at 105 °C for 2 hr. Place the dried samples in a desiccator for 1 hr and weight (*note2*).

Note1 In practice, a crucible from a previous determination is used

Note2 The sample shall be considered oven-dry when, the decrease in weight of consecutive weightings is 0.0005 g or less. Succeeding dry periods shall be not less than 1 hr.

3. ***Volatile matter*** Heat the muffle furnace to 950 °C. Preheat the crucibles used for the moisture determination, with lids in place and containing the sample, as follows: with the furnace door oven, for 2 min on the outer ledge of the furnace (300 °C) and then for 3 min on the edge of the furnace (500 °C) (*Note3*). Then move the samples to the rare of the furnace for 6 min with the muffle door closed. Watch the samples through a small peep-hole in the muffle door. If sparking occurs, results will be in error (*Note4*). Cool the samples in a desiccator for 1 hr and weigh.

    Note3 Individual nichrome wire baskets to hold the crucibles are convenient.

Note4 If the speaking sample dose not check the results of its nonsparking duplicate within ±0.5%, the analysis shall be repeated.

4. ***Ash*** Place the lids and the uncovered crucible used for the volatile matter determination, and containing the sample in the muffle furnace at 750 °C for 6 hr. Cool the crucibles with lids in place in a desiccator for 1 hr and weigh. Repeat burning of the sample until a succeeding 1 hr period of heating results in a loss of less than 0.0005 g.

Calculation

1. Calculate the percentage of moisture in the sample as follows:

   Calculate the moisture content as follows:

$$\text{Moisture, \%} = [(A - B) / A] \times 100$$

Where:

A = grams of air-dry sample used, and

B = grams of sample after drying at 105 °C

2. Calculate the percentage of volatile matter content in the sample as follows:

$$\text{Volatile matter, \%} = [(B - C) / B] \times 100$$

Where:

C = grams of sample after drying at 950 °C.

3. Calculate the percentage of ash in the sample as follows:

$$\text{Ash, \%} = (D / B) \times 100$$

Where

D = grams of residue.

Appendix B.2

Standard Test Method for Apparent Density of activated Carbon (ASTM D 1884-89)

This test method covers the determination of the apparent density (bulk density) of granular activated carbon. It is determined on granular sample by measuring the volume packed by a free fall from a vibrating feeder into a 10 mL graduated cylinder and weighing the known volume. For purposes of this test method, granular activated carbon is defined as a minimum of 90% being larger than 80 mesh.

Procedure

1. Dry an adequate sample of the carbon to be tested to constant weight at $150 \pm 5\ ^{o}$C.
2. Carefully place a representative sample of the activated carbon into the feed funnel so that the material does not prematurely flow into the graduated cylinder.
3. Fill the cylinder at a uniform rate up to 10 mL mark.
4. Transfer the contents from the cylinder to a balance pan and weight to the nearest 0.1 g.

Calculation

Calculate the bulk density as follows :

Bulk density, g/ml = weight of activated carbon/10

Appendix B.3

Standard Test Method for Moisture in Activated Carbon (ASTM D 2867-95)

These test methods for the determination of the moisture content of activated carbon, for this work used the oven-drying method. The oven-drying method is used when water is the only volatile material present and is in significant quantities, and the activated carbon is not heat-sensitive (some activated carbons can ignite spontaneously at temperatures as low as 150 °C) and weighed accurately. The capsule is opened and placed with the lid in a preheated oven. The sample is dried to constant weight then removed from the oven and with the capsule closed, cooled to ambient temperature. The closed capsule is weighed again accurately. The weight loss expressed as a percentage of the weight of the original sample.

Procedure (for Activated carbon Passing A No. 50 Sieve)

1. Dip out with a spoon or spatula from the sample bottle a 1 to 2 g representation sample. Put this into a predried tared capsule with lid, close and weight at once to the nearest 0.5 mg. The depth of the carbon in the capsule must not exceed 1.25 cm.
2. Remove the cover and place the capsule and cover in a preheated forced circulation oven (at 145 to 155 °C). Close the oven and dry to constant weigh (3 hr normally sufficient). Open the oven and cover the capsules quickly. Cool in desiccator to ambient temperature and weigh.

Calculation

Calculate the moisture content as follows:

$$\text{Moisture, weight \%} = [(C - D) / (C - B)] \times 100$$

Where:

B = weight of capsule with cover, g

C = weight of capsule with cover plus original sample, g, an

D = weight of capsule with cover plus dried sample, g.

Appendix B.4

Standard Test Method for Total Ash content of Activated Carbon (ASTM D 2866-94)

This test method describes a procedure for the determination of total ash content of activated carbon. An accurately weighed sample of dried activated carbon is placed in a controlled-temperature muffle furnace for a period of several hours. When content weight has been achieved, the crucible is cooled to ambient temperature in a decentage of the weight of the original carbon sample.

Procedure

1.Ignite the crucible in the muffle furnace at 650 ± 25 °C for 1 hr Place the crucible in the desiccator. Cool to room temperature and weight to the nearest 0.1 mg.

2.Dry an adequate sample of activated carbon to constant weight at 150 ± 5 °C (3 hr is usually sufficient).

3. Weigh out to the nearest 0.1 mg. Sufficient dried activated carbon, so that the estimated amount of ash will be 0.1 g, into the ignited crucible and place the crucible in the furnace at 650 ± 25 °C. Ashing will require from 3 to 16 hr, depending on the size and type of activated carbon. Ashing can be considered complete when constant weight is achieved.

4. Place the crucible in the desiccator and allow to cool to room temperature. After the sample has cooled in the desiccator, admit air slowly to avoid loss of ash from the crucible. Weigh to the nearest 0.1 mg.

Calculation

Calculate the ash content as follows:

$$\text{Total ash, \%} = [(D - B)] / (C - B)] \times 100$$

Where:

B = weight of crucible, g,

C = weight of crucible plus original sample, g, and

D = weight of crucible plus ashed sample, g .

Appendix B.5

Standard Test method for Determination of Iodine Number of Activated Carbon (ASTM D 4607-94)

This test method covers the determination of the relative activation level of unused of reactivated carbons by adsorption of iodine from aqueous solution. The amount of amount of iodine absorbed (in milligrams) by 1 g of carbon using test conditions listed herein is called the iodine number.

This test method is based upon a three-point adsorption isotherm. A standard iodine solution is treated with three different weights of activated carbon under specified conditions. The carbon treated solution are filtered to separate the carbon from the treated iodine solution (filtrate). Iodine remaining in the filtrate is measured by titration. The amount of iodine removed per gram of carbon is determined for each carbon dosage and the resulting data used to plot an adsorption isotherm. The amount of iodine adsorbed (in milligrams) per gram of carbon at a residual iodine concentration of 0.02 *N* is reported as the iodine number.

1. Preparation of solutions

1.1 *Hydrochloric Acid Solution* (5 % by weight). Add 70 ml of concentrated hydrocholic acid to 500 ml of distilled water and mix well. A graduated cylinder may be used for measurement of volume.

1.2 *Sodium Thiosulfate* (0.100 N). Dissolve 24.820 g of sodium thiosulfate in appropximately 75 ± 25 ml of freshly boiled distilled water. Add 0.10 ± 0.01 g of sodium carbonate to minimize bacterial decomposition of the thiosulfate solution. Quantitatilvely transfer the mixture to a 1 L volumetric flask and dilute to the mark. Allow the solution to stand at least 4 days before standardizing. The solution should be stored in an amber bottle.

1.3 *Standard Iodine Solution* (0.100 ± 0.001 N). Weigh 12.700 g of iodine and 19.100 g of potassium iodine (KI) into a beaker. Mix the dry iodine and potassium iodine. Add 2 to 5 ml of water to the beaker and stir well. Continue adding small increment of water (approximately 5 ml each) while stirring until the total volume is 50 To 60 ml. Allow the solution into stand a minimum of 4 to ensure that all crystals are thoroughly dissolved. Occasional stirring during this 4 hr period will aid in the dissolution. Quantitatively transfer to a 1 L volumetric flask and fill to the mark with distilled water. It is important that the standard iodine solution has an iodine-to-iodine weight ratio of 1.5 to 1. Store the solution in an amber bottle.

1.4 *Potassium Iodate solution* (0.1000 N). Dry 4 or more grams of primary standard grads potassium iodate (KIO_3) at 110 ± 5 °C for 2 hr and cool to room temperature in a desicator. Dissolve 3.5667 ± 0.1 mg of the dry potassium iodate in about 100 ml of distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. Mix thoroughly and store in a glass- stoppered bottle.

1.5 *Starch Solution.* Mix 1.0 ± 0.5 g of starch with 5 to 10 ml of cold water to make a paste.

Add an additional 25 ± 0.5 g of water while stirring to the starch paste. Pour the mixture, while stirring, into 1 L of boiling water add boil for 4 to 5 min. This solution should be made fresh daily.

2. Standardization of solutions

2.1 *Standardization of 0.100 N Sodium Thiosulfate*. Pipet 25.0 ml of potassium iodate (KIO_3) solution from 1.2 into a 250-ml titration (or wide-mouthed Erlenmeyer) flask. Add 2.00 ± 0.01 g of potassium iodide (KI) to the flask and shake the flask to dissolve the potassium iodide crystals. Pipet 5.0 ml of concentrated hydrochloric acid into the flask. Titrated the free iodine with sodium thiosulfate solution until a light yellow color is observed in the flask. Add a few drops of starch indicator (1.5) and continue the titration dropwise until one dropwise until one drop produces a colorless solution. Determine sodium thiosulfate normality as follows:

$$N_1 \ = (P \quad R) / S$$

Where :

N_1 = sodium thiosulfate, N,
P = potassium iodate, ml,
R = potassium iodate, N, and
S = sodium thiosulfate, ml.

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceeds 0.003 *N*.

2.2 *Standardization of 0.100 ±0.001 N Iodine solution.* Pipet 25.0 ml of iodine solution (1.3) into a 250-mL wide mouthed Erlenmeyer flask. Tritrate with standardized sodium thiosulfate (2.1) until the iodine solution is a light yellow color. Add a few drops of starch indicator (1.5) and continue the titration dropwise until one drop produces a colorless solution. Determine iodine solution normality as follows:

$$N_2 = (\ S \quad N_1) / \quad I$$

Where :

N_2 = iodine, N,
S = sodium thiosulfate, ml,
N_1 = sodium thiosulfate, N, and
I = iodine, ml.

The titration step should be done in triplicate and the normality results averaged. Additional replications should be done if the range of values exceed 0.003 *N*. The iodine solution concentration must be 0.100 ± 0.001 *N*. If this requirement is not met, repeat 1.3 and 2.2.

3. Procedure

3.1 The procedure applies to either powdered or granular activated carbon. When granular carbon is to be tested, grind a representative sample of carbon until 60 wt % (or more will pass through a 325-mesh screen) and 95 wt % or more will pass through a 100-mesh screen (U.S. sieve series, see specification E 11). Carbon received in the powdered from may need additional grinding to meet the particle size requirement given above.

3.2 Dry the ground carbon from 3.1 in accordance with test method D 2867. Cool the dry carbon to room temperature in a desiccator.

3.3 Determination of iodine number requires an estimation of three carbon dosages. Section 4 and **Table B.5.1** describes how to estimate the carbon dosages to be used. After estimating carbon dosages, weight three appropriate amounts of dry carbon to the nearest milligram. Transfer each weighed sample of carbon to a clean, dry 250-mL. Erlenmeyer flask equipped with a ground glass stopper.

3.4 Pipet 10.0 ml of 5 wt % hydrochloric acid solution into each flask containing carbon. Stopper each flask and swirl gently until the carbon is completely wetted. Loosen the stoppers to vent the flasks, place on a hot plate in a fume hood, and bring the contents to a boil. Allow to boil gently for 30 ± 2 s to remove any sulfur which may interfere whit the test results. Remove the flasks from hot plate and cool to room temperature.

3.5 Pipet 100.0 ml of 0.100 *N* iodine solution into each flask. Standardize the solution just prior to use. Stagger the addition of iodine to the three flasks so that no delays are encountered in handling. Immediately stopper the flasks, and shake the contents vigorously for 30 ± 1 s. Quickly filter each mixture by gravity through one sheet of folded filter paper (Whatman No. 2V or equivalent) into a beaker. Filtration equipment must be prepared in advance so no delay is encountered in filtering the samples.

3.6 For each filtrate, use the first 20 to 30 ml to rinse a pipet. Discard the rinse portion. Use clean beakers to collect the remaining filtrates. Mix each filtrate by swirling the beaker and pipet 50.0 ml of each filtrate into a clean 250-mL Erlenmeyer flask. Titrate each filtrate with standardized 0.100 *N* sodium thiosulfate solution until the solution is a pale yellow. Add 2 mL of the starch indicator solution and continue The titration with sodium thiosulfate until one drop produces a colorless solution. Record the volume of sodium thiosulfate used.

4. Calculation

4.1 The capacity of carbon for any adsorbate is dependent upon the concentration of the adsorbate in solution. The concentrations of the standard iodine solution and filtrate must be specified or known. This is necessary to determine an appropriate carbon weight to produce final concentrations agreeing with the definition of iodine number. The amount of carbon sample to be used in the determination is governed by the activity of the carbon. If filtrate normalities (C) are not within the range of 0.008 *N* to 0.040 *N*, repeat the produre using different carbon weights.

4.2 Two calculations are required for each carbon dosage, as *X/M* and *C*

4.2.1 To calculate the value of *X/M*, first derive the following values:

$$A = (N_2)\ (12693.0)$$

Where:

N_2 = iodine, *N* (from 2.2)

$$B = (N_1)\ (126.93)$$

Where:

N_1 = sodium thiosulfate, *N* (from 2.1)

$$DF = (I + H) / F$$

Where:

DF = dilution factor,

I = iodine, ml (from 2.2),

H = 5% hydrochloric acid used, ml, and

F = filtrate, ml.

For example, if 10 ml of HCl and 50 ml of filtrate are used:

$DF + (100+10) / 50 = 2.2$

4.2.1.1 Calculate the value of X/M as follows:

$$X/M = [A - (DF)(B)(S)] / M$$

Where:

X/M = iodine absorsed per gram of carbon, mg/g,

S = sodium thiosulfate, N, and

M = carbon used, g.

4.2.2 Calculate the value of C as follows:

$$C = (N_1 S) / F$$

Where:

C = residual filtrate, N,

N_1 = sodium thiosulfate, ml, and

F = filrate, ml.

4.3 Using logarithmic paper, plot X/M (as the ordinate) versus C (as the abscissa) for each of the three carbon dosages. Calculate the least squares fit for the three points and plot. The iodine number is the X/M value at a residual iodine concentration (C) of 0.02 N. The regression coefficient for the least squares fit should be grater than 0.995.

4.4 Carbon dosage may be estimated as follows:

$$M = [A - (DF)(C)(126.93)(50)] / E$$

Where:

M = carbon, g,

A = (N_2) (12693.0),

DF = dilution factor (see 4.2.1)

C = residual iodine, and

E = estimated iodine number of the carbon.

Three carbon dosage are calculated using three values of C (usually 0.01,0.02 , and 0.03)

Table B.5.1 Find M for calculation iodine number by using ASTM D4607-86.

Appendix B.6

Standard testing method of Methylene Blue Number of Activated Carbon (JIS K 1470-1991)

1. Preparation of solutions

1.1 *Potassium dihydrogen phosphate solution* – Dry of potassium dihydrogen phosphate (KH_2PO_4) in the oven at 110-120 °C for 2 hr and cool to room temperature in a desicator. Dissovle 9.07 g of KH_2PO_4 dry with distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water.

1.2 *Disodium hydrogen phosphate solution*- Dry of disodium hydrogen phosphate (NA_2HPO_4) in the oven at 110-120 °C for 2 hr and cool to room temperature in a desicator. Dissolve 23.88 g of dry NA_2HPO_4 with distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with distilled water.

1.3 *Buffer solution* – Mix 400 ml of 1.1 and 600 ml of 1.2. The pH of this solution is approximately 7.

1.4 *Standard methylene blue solution* – Dry of methylene blue in the oven at 105 ± 5 °C For 4 hr and cool to room temperature in a desicator. Dissolve 1.2 g of dry methylene blue with buffer solution. Quantitatively transfer to a 1-L volumetric flask and fill to the mark with buffer solution.

2. Procedure

2.1Dry of activated carbon at 150 ± 5 °C (3 hr is usually sufficient).

2.2 Weigh the specified amount (note 1) of activated carbon to the nearest 1 mg, transfer to an Erlenmeyer flask with ground-in stopper 100 ml, and add methylene blue solution 25 ml.

2.3 Shake at room temperature using a shaker for 30 min.

2.4 Take methylene blue solution 10 ml into one mark volumetric flask 50 ml, and add buffer solution up to the marked line. Further, take its 5 ml into other one mark volumetric flask 500 ml, and add buffer solution up to the marked line. In this case the concentration of methylene blue solution is 0.24 mg/l.

2.5 Measure the absorbance at wavelength of 665 nm with contrasting to buffer solution.

Note 1 Weight the sample by dividing into three stage degree so that the mass interval dose not exceed 0.02 g corresponding to anticipated methylene blue adsorption performance to the sample 0.1 to 0.3 g.

3.Preparation of calibration curve

3.1 Take methylene blue solution 10 ml into one mark volumetric flask 50 ml, and add buffer solution up to the marked line. From this solution, take 5, 10, 25 and 50 ml into respective one mark volumetric flask 500 ml, and add buffer solution up to the marked line.

3.2 For these solution, prepare the relation curve between the concentration of methylene blue solution (0.24 to 2.4 mg/l) and the absorbance at 665 nm in wavelength and obtain from this the remaining concentration of methylene blue.

4.Calculation Using the remaining concentration of methylene blue obtain in **3**, the methylene blue amount (mg/g) shall be calculated using the following formula.

$$Q = \frac{(1200-C)\ (25/1000)}{S}$$

Where : Q = Methylene blue adsorption amount (mg/g),
C = remaining concentration of methylene blue (mg/l),
S = mass of activated carbon (g) and
1200 = concentration of methylene blue soultion (mg/l).

5.Preparation of adsorption isotherm in methylene blue solution. Plot the remaining concentration of methylene blue solution obtained in **3** on the abscissa and the adsorption amount of methylene blue obtained using the calculation method of **4** on the ordinate of both logarithm graph and prepare the adsorption isotherm. From the adsorption isotherm obtain the methylene blue amount (mg/g) of sample when the remaining concentration of methylene blue as the methylene blue adsorption performance is 0.24 mg/l.

Appendix B.7

Standard Test Methods for Carbon Black-Surface area by multipoint B.E.T. Nitrogen Adsorption (ASTM D 4820-96a)

A carbon sample is placed in a known volume cell and evaluated to less than 5 milliliter of vacuum. Using the ideal gas equation, the volume of nitrogen required to give a predetermined relative pressure is calculated and dosed into the sample cell. Any additional nitrogen required to attain this relative pressure is due to adsorption by the carbon. Based on the volume of nitrogen adsorbed at various relative pressures, the surface area is calculated.

Theory of Test Method

The determination of surface area from the B.E.T. theory is a straight forward application of the B.E.T. equation :

$$\frac{1}{V\,[(Po/P) - 1]} = \frac{1}{V_M C} + \frac{C - 1}{V_M C} \times \frac{P}{Po}$$

Where :

V = volume of nitrogen adsorbed, cm3

P = pressure, kPa,

Po = saturation vapor pressure of nitrogem, kPa,

V_M = volume of nitrogen that cover one monomolecular layer, cm^3, and

C = B.E.T. constant.

A plot of 1 / V [(Po/P) – 1] versus P / Po will usually yied a straight line in the range 0.05 to 0.35 Solving the B.E.T. equation for V_M gives:

$$V_M = \frac{1}{M + B}$$

Where:

M = slop of straight line, and

B = y-intercept.

Sample Preparation

1. Place a clean sample tube on the degassing station and heat at 150 °C for 0.5 hr at a Pressure below 2.7 pa (20 umHg). The insection of a glass rod into the sample tube stem will reduce the void volume of the stem, thus improving testing precision.

2. Cool the sample tube to room temperature, then backfill, preferably with helium to atmospheric pressure. Place a stopper on the sample tube and weight it to nearest 0.0001 g and record as mass *A*.

3. For samples of unknown surface area, place approximately 0.1 g of carbon in the sample tube clean the sample tube stem with a pipe cleaner.

4. Place the sample tube containing the carbon on the degassing station and open the vacuum valve

5. Place the heating mantle on the sample cell and heat at 150 °C for 1 hr or longer to obtain and hold a pressure less than 2.7 Pa (20 umHg).

6. Remove the heating mantle and allow the sample sell to cool to room temperature. Backfill the sample tube with helium to atmospheric pressure, remove from the degassing station, and close it with a stopper.

Sample analysis

1. Place the sample tube containing the carbon on the nitrogen surface area analyzer.
2. Initial the experiment. The following experiment steps, necessary to attain accurate Results, can be automatically determined by most automated nitrogen surface area analyzers.

2.1 Leak Teat – The vacuum volumetric relies on pressure measurements to determine the surface area of carbon. Any leaks in the system will result in erroneous surface area measurements. A minimum of a 2 min leak teat of this time interval will result in the absorption of the experiment.

2.2 *Transducer Linearization* – If separate sample and transducer manifolds are utilized by the testing equipment, it is necessary to zero and linearize the transducers prior to each experiment.

2.3 *Sample Cell Volume* – In determining the void volume of the sample cell, both warm zone (section submersed in liquid nitrogen) must be measured prior to each analysis. Non-ideality gas corrections are applied to the volume of gas in the cold zone

2.4 *Saturated Vapor Pressure* (Po) – The saturated vapor pressure of nitrogen is affected by purity of the liquid nitrogen and ambient pressure. Dissolved impurities In the liquid N_2 will usually cause the bath temperature to in crease sufficiently to cause a 1.4 to 2.7 kPa (10 to 20 mmHg) increase in theoretical vapor pressure. Often, Po is assumed to be 103 kPa (775 mmHg); however, for maximum accuracy the actual Po should bi measured.

3. Once the above conditions are measured, volumes of pure nitrogen are calculates, measured, and dosed into the sample cell. This process is repeated until equilibrium conditions are satisfied at the desired relative pressure. The summation of the dose volumes required to reach a particular relative pressure constitute the adsorption volume pressures of 0.05 to 0.30. A minimum of 5 relative pressures are recommended

4. Backfill the sample tube at ambient temperature with helium to atmospheric pressure. Remove the sample tube from the instrument, stopper it, and weigh it to the nearest 0.0001 g and record as mass *B*.

5. Nitrogen adsorbed by the carbon at the various relative pressure is used to prepare the B.E.T. plot. The data points that give the best straight line are used to calculate the stop and y-intercept. The slope and y-intercept are used to calculate the surface area. For examples of how to select the proper relative pressure range.

6. A B.E.T. plot that yields a negative y-intercept could be indicative of the presence of microprobes (< 3 nm diameter), but other factors can produce a negative y-intercept.

The surface area is calculated from the pressure range that yields the highest correlation coefficient and positive y-intercept.

Calculation

1. Calculate the sample mass as follows :

$$S = B - A$$

Where :

S = sample mass, g,

A = mass of sample tube, stem, and stopper, and

B = mass of sample tube, stem, stopper, and sample after analysis.

2. Calculate the nitrogen surface area (NSA) to the nearest 0.1 x 10^3 m^2/kg (0.1 m^2/g) as follows :

$$NSA = \frac{V_M N A_{CS}}{22\ 400 \times S}$$

where :

N = Avagadro's number, 6.023 x 10^{23}

A_{CS} = Cross-section area of nitrogen molecule, 16.2 x 10^{-20} m^2/moleculr, and

22 400 = number of cm^3 occupied by one mole of gas at STP.

VITA

Phawika Chuenklang was born on May 22, 1975 in Bangkok, Thailand. She received Bachelor Degree of Industrial Chemistry at King Mongkut's Institute of Technology North Bangkok in 1996. She continue her Master's study at Program of Petrochemistry and Polymer Science, Faculty of Science Chulalongkorn University in 1999 and completed the program in 2001. She worked as Technical sales at Intergoods CO., Ltd.