

PRODUCTION OF ACTIVATED CARBON FROM EUCALYPTUS BARK  
(*CAMALDULENSIS DEHN*) BY PHYSICAL ACTIVATION  
FOR REMOVAL OF LEAD



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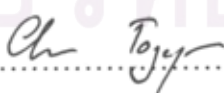
  
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งานวิจัยนี้เป็นการผลิตถ่านกัมมันต์จากเปลือกไม้ยูคาลิปตัส *Camaldulensis Dehn.* ด้วยวิธีการกระตุ้นทางกายภาพ แบ่งการทดลองเป็นสองขั้นตอน ขั้นตอนแรกเป็นการคาร์บอนไนซ์ เพื่อศึกษาถึงผลของอุณหภูมิและเวลา พบว่า ภาวะที่เหมาะสมในการคาร์บอนไนซ์คือ ที่อุณหภูมิ 500 องศาเซลเซียส เวลา 45 นาที ขั้นตอนที่สองเป็นการกระตุ้นถ่านชาร์ โดยศึกษาถึงผลของอุณหภูมิ เวลา และชนิดของแก๊สในการกระตุ้น ภาวะที่เหมาะสมในการกระตุ้นของถ่านชาร์โดยใช้ไอน้ำเป็นตัวกระตุ้น คือ ที่อุณหภูมิ 900 องศาเซลเซียส เป็นเวลา 120 นาที ลักษณะสมบัติของถ่านกัมมันต์ที่ได้ มีค่าความหนาแน่นเชิงปริมาตร 0.37 กรัมต่อลูกบาศก์เซนติเมตร ปริมาณแฉ่ำร้อยละ 37.3 ผลิตกัณฑ์ร้อยละ 52.5 ค่าการดูดซับไอโอดีน 694 มิลลิกรัมต่อกรัม พื้นที่ผิวแบบบีอีที ( $S_{BET}$ ) 794 ตารางเมตรต่อกรัม และที่สภาวะเดียวกันเมื่อใช้แก๊สคาร์บอนไดออกไซด์เป็นตัวกระตุ้น ได้ลักษณะสมบัติของถ่านกัมมันต์คือ ปริมาณแฉ่ำร้อยละ 30.9 ผลิตกัณฑ์ร้อยละ 58.5 ค่าการดูดซับไอโอดีน 352 มิลลิกรัมต่อกรัม พื้นที่ผิวแบบบีอีที ( $S_{BET}$ ) 274 ตารางเมตรต่อกรัม เมื่อนำถ่านกัมมันต์ที่ได้จากการทดลองดูดซับตะกั่วพบว่า ความสามารถในการดูดซับตะกั่วสูงสุด จะเกิดที่ค่าความเป็นกรดต่างเท่ากับ 4 การดูดซับเข้าสู่สมดุลภายในเวลา 30 นาที ตลอดช่วงความเข้มข้นเริ่มต้นของโลหะหนักที่ใช้ในการทดลองที่ 10-50 มิลลิกรัมต่อลิตร และไอโซเทอมการดูดซับแบบ Langmuir เหมาะสมในการทดลองนี้มากกว่าไอโซเทอมการดูดซับแบบ Freundlich

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This research investigated the production of activated carbon from *Eucalyptus camaldulensis Dehn* bark by physical activation. The experiment was composed of two steps: the first step was the carbonization and the second was the activation. For the carbonization, the optimal condition was found to be 500°C and 45 minutes. The optimal activation condition with steam as activating agent was at 900°C for 120 minutes using N<sub>2</sub> gas as a carrier at the flow rate of 200 cm<sup>3</sup> min<sup>-1</sup> where the properties of the prepared activated carbon were: bulk density 0.37 g cm<sup>-3</sup>, ash content 37.3%, yield 52.5%, iodine number 694 mg g<sup>-1</sup> and BET surface area 794 m<sup>2</sup> g<sup>-1</sup>. At the same activation condition, change activating agent to carbon dioxide instead, the properties of the prepared activated carbon were: bulk density 0.39 g cm<sup>-3</sup>, ash content 30.9%, yield 58.5%, iodine number 352 mg g<sup>-1</sup> and BET surface area 274 m<sup>2</sup> g<sup>-1</sup>. The activated carbon product from steam activation process was tested for its adsorption capacities for Pb(II). Experiments demonstrated that Pb(II) was best adsorbed at pH 4 where the adsorption reached equilibrium within 30 minutes for the whole range of initial heavy metal concentrations investigated here (10-50 mg L<sup>-1</sup>). The adsorption isotherm followed Langmuir better than Freundlich models where the maximum sorption capacity was 54.6 mg g<sup>-1</sup>.

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# CHAPTER I

## INTRODUCTION

### 1.1 Motivation

Urbanization and industrialization inevitably cause wastewater pollution, including wastewater contaminated with heavy metals. Lead, in particular, is a common metal used in various products. Contamination with lead is often found in both wastewater and soil. The uptake of lead can impair the central nervous system and damage the cells that create the blood-brain barrier to protect the brain from many harmful chemicals. Several treatment processes can be used for removing lead from wastewater, e.g. chemical reduction electrodepositing, metal coagulation, ion exchange and adsorption by activated carbon. The selection of the treatment technique depends on the characteristics of wastewater. For instance, wastewater with high level of lead might be treated with coagulation whereas low level contamination can be better treated with ion exchange or adsorption. Activated carbon is one common adsorbent for lead and many other metals due to its durability and cost effectiveness (Kongsuwan et al., 2009).

In principle, the methods for preparing an activated carbon can be divided into two categories, i.e. chemical and physical activations. For the chemical activation, the raw material is impregnated with activation agents such as phosphoric acid, potassium hydroxide, zinc chloride, etc. and heated at elevated temperature to simultaneously carbonize and activate the carbon. Although this requires lower temperature when compared with the physical means, it suffers from its inherited disadvantages, e.g. the generation of contaminated wastewater (Daifullah, 2004) and impurities derived from the activating agent, which may affect the chemical properties of the activated carbon (Gomez-serrano et al., 2005). For the physical activation, the raw material is carbonized in an inert atmosphere at a temperature below 700°C and then activated by steam or carbon dioxide at temperatures range from 800 to 1000°C. This high temperature requirement is compensated by the elimination of chemical contaminants and shorter production time (Laine and Yunes, 1992), and these make it more environmental attractive.

At present, the domestic capacity for the production of activated carbon still does not match the demand side which requires that activated carbon be imported. Costs of activated carbon imported to Thailand in the years 2007 and 2008 were approx. 730 million and 1,236 million baht, respectively (The Customs Department, 2004 and 2005). There is therefore a large demand for the research for alternative raw materials for the activated carbon.

The pulp mill has generated a large quantity of eucalyptus bark. More than 10 tons per day of Eucalyptus bark has been produced alone from one particular commercial plantation area in Prachinburi province, Thailand. Preliminary analysis revealed that eucalyptus bark has relatively high carbon content and low inorganic content which makes it suitable for preparing activated carbon (Gonzalez et al., 2009). In addition, our previous work has shown that this bark could well be converted to activated carbon using chemical activation (Patnukao et al., 2008; Sarin et al., 2006). Hence, this study aims to extend the research finding to cover the mechanism of physical technique in the preparation of activated carbon. The activation with steam and carbon dioxide will therefore be investigated. The final product will be tested for its capacity in the treatment of lead contaminating concocted wastewater.

## **1.2 Objectives**

The objectives of this study are:

1. To produce activated carbon from eucalyptus bark by physical activation
2. To remove lead from synthetic wastewater by the derived activated carbon

## **1.3 Hypotheses**

1. Eucalyptus bark can be converted to activated through physical means such as steam or carbon dioxide activation.
2. Steam activation gives a better quality activated carbon product in terms of active surface area than carbon dioxide activation.
3. Activated carbon from eucalyptus bark has adsorption capacity for positively charged metals such as lead.

#### 1.4 Scopes of the research

1. This study was an experimental study in laboratory scale.
2. The optimal conditions of preparing activated carbon from eucalyptus bark were investigated. The variables of this study include
  - Carbonization temperature : 450, 500, 550 and 600°C
  - Carbonization time : 30, 45, 60, 90 and 120 min
  - Type of activated gas : steam and carbon dioxide
  - Activation temperature : 850, 900, 950 °C
  - Activation time : 60, 90, 120 min
3. Physical and chemical properties of activated carbon were indicated by
  - Elemental analysis: C, H and N content.
  - Proximate analysis: fixed carbon, volatile matters, ash and moisture
  - Surface area: BET method and iodine number
  - Pore volume: micropore and mesopore volume
  - Adsorbent characteristic: apparent (bulk) density and yield
  - Adsorbent structure analysis: X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM)
  - Functional group: Fourier Transform InfraRed (FTIR)
4. Lead adsorption of activated carbons derived from eucalyptus bark was evaluated with batch adsorption experiments.

## **CHAPTER II**

### **THEORY AND LITERATURE REVIEWS**

#### **2.1 General knowledge of Eucalyptus wood**

Eucalyptus has been grown in Thailand for over 100 years ago, but only after the year 1970 on plantation scale. Advantages of eucalyptus are easy growth, good survival, tolerant to various climates and soil types (Ngernyen et al., 2006). Eucalyptus belongs to the myrtle (Myrtaceae) family. Although many species of eucalyptus are introduced into Thailand, only a few species and provenances show promising survival and growth e.g. *E. camaldulensis*. It is adaptable to saline soils in the northeast Thailand, and tolerates a variety of climatic conditions (Royal Forest Department [RFD], 2009). The whole eucalyptus tree could be used for fuel, pulp and paper, furniture, charcoal and oil.

The eucalyptus bark consists of two parts, smooth-bark and rough-bark. The smooth-bark is the outer part leaving a smooth surface. This part remains on the tree even it is dead. The rough-bark is the inner layer which is the focus of this work for the production activated carbon.

#### **2.2 Lead**

Lead is a bluish-white lustrous metal. Its characteristics are very soft, highly malleable, ductile, and relatively poor electrical conductivity. Lead and lead compounds are highly corrosive resistance but tarnish upon exposure to the air. Lead compounds comprise several products including paints, ceramics, pipes, solders, gasoline, batteries, cosmetics, etc. Exposure of excessive lead level causes a variety of neurological disorders such as lack of muscular coordination, convulsions and coma, on the other hand, lower lead level associates with measurable changes in children's mental development and behavior. These include hyperactivity; deficits in fine motor function, hand-eye coordination, and reaction time; and lowered performance on intelligence tests. Chronic exposure in adults results in increasing of blood pressure, decreased fertility, cataracts, nerve disorders, muscle and joint pain, and memory problems.



The available methods to remove lead and lead compounds include: ion exchange, electrochemical reduction, evaporation, reverse osmosis, adsorption and direct precipitation (Boudrahem et al., 2009). Chemical precipitation, in particular, is the most prevalent method but not suitable for removing low concentration of heavy metal ions. Adsorption process promises in this regard as opposed to more conventional chemical precipitation because it achieves higher level removal in wider range of solution. This means that the adsorption with the selection of suitable adsorbents can be an effective technique for the removal of heavy metals from wastewater (Rafatullaha et al., 2009).

### **2.3 Activated carbon**

Activated carbon, sometimes called activated charcoal, is a form of carbonaceous material that has been processed to highly develop internal surface area and porosity which can be described as solid sponges (Zanzi et al., 2001). Microporosity in the activated carbon is most important for adsorption ability and widely used to indicate the quality of activated carbon. Generally, one gram of activated carbon achieves a surface area of over 500 m<sup>2</sup>, as determined typically by nitrogen gas adsorption. Activated carbon can be classified based on its physical characteristics as follows.

#### **2.3.1 Powdered activated carbon (PAC)**

Traditionally, activated carbons are made in a powder form with a size range between 0.15 and 0.25 mm. PAC is not commonly used in a dedicated vessel, owing to the high head-loss that would occur. It is beneficial to reduce the concentration of trace organics in drinking water such as pesticides (Humbert et al., 2008). One of the main advantages of PAC is low capital cost, however, its applicability is limited to the low concentration of organic materials due to the short contact time (Kim et al., 2008). Additionally, handling and disposal of PAC could be difficult (Areerachakul et al., 2007).

#### **2.3.2 Granular activated carbon (GAC)**

Granular activated carbon (GAC) is generally associated with small pore diameter and large internal surface area. This forms irregular shaped particles with size ranging from 0.2-5.0 mm and they are considered more versatile and command a larger percentage of the carbon market (Activated Carbon Markets, 1994). About 80%

of the GAC produced worldwide is used in liquid-phase purifications, and the rest is used in gas-phase applications (Usmani et al., 1994).

### 2.3.3 Pellets or extruded activated carbon

The shape of extruded and cylindrical activated carbon appears with diameters from 0.8 to 45 mm. It is mainly required for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

## 2.4 Raw materials for the production of activated carbon

Activated carbons can be prepared from several raw materials, which should be abundant and cheap, with high carbon content and low volatile content like wood, coal, lignite, and coconut shells. The properties of manufactured activated carbon depend on the type and properties of the raw material used. Some of the properties of raw materials suitable for the production of activated carbon are summarized below:

- low organic volatile content
- high carbon content
- high lignin content
- inexpensive and efficient use of resources
- high and stable properties

Several raw materials were attractive to produce activated carbon as illustrates in Table 2.1. It can be seen that these materials have high content of fixed carbon and low content of ash, nitrogen and sulfur, which is interesting with respect to their applications in gasification and pyrolysis processes (Gonzalez et al., 2009).

In the recent years, many agricultural by-products have been used as sources for activated carbons production such as cherry tree (Ioannidou et al., 2007), Coconut shells (Li et al., 2009), Coffee endocarp (Nabais et al., 2008), olive stones (Gonzalez et al., 2009), oil palm stones (Cagnon et al., 2009), and eucalyptus wood (Ngernyen et al., 2006). They are suited for activated carbon manufacture due to their pyrolytic transformation into porous coke which produces an economically justifiable yield. Suitable adsorbent properties (adsorption capacity, hardness, and granularity) require the use of mechanically stable cokes with a small fraction of macropores (Bouchelta et al., 2008).

Table 2.1 Properties of raw materials for the production of activated carbon

<b>Raw materials</b>	<b>Moisture (%)</b>	<b>Ash (%)</b>	<b>Volatiles (%)</b>	<b>C (%)</b>	<b>H (%)</b>	<b>N (%)</b>	<b>S (%)</b>	<b>References</b>
Almond tree	10.60	1.20	72.20	51.30	6.50	0.80	0.04	Gonzalez et al., 2009
Corn cobs	-	0.9	80.2	48.89	6.38	0.18	0.00	Aworn et al., 2009
Eucalyptus bark	10.50	1.35	76.05	41.36	4.67	-	-	Patnukao et al., 2007
Eucalyptus wood	4.1	1.2	76.4	-	-	-	-	Ngernyen et al., 2006
Olive stone	10.40	1.40	74.40	44.80	6.00	0.10	0.01	Gonzalez et al., 2009
Plum stones	3.8	0.9	-	50.7	6.3	2.1	<0.3	Cagnon et al., 2009

## 2.5 Production of activated carbon

The preparation of activated carbon can be mainly classified into two processes: chemical activation and physical activation. The nature of the precursor, activation method, and activation conditions determine the characteristics of porosity in activated carbons, including pore size distribution, shapes of pores, and surface chemistry (Sentorun-Shalaby et al., 2006). The detail of chemical and physical activation is presented below:

### 2.5.1 Chemical activation

Chemical activation is usually limited to woody precursors. This process involves carbonizing the parent materials after impregnation with, e.g., phosphoric acid (Castro et al., 2000), sulphuric acid, potassium carbonate (Hameed et al., 2008), potassium hydroxide (Tseng et al., 2008), sodium chloride (Khuysangaain, 2001), and zinc chloride (Aravindhana et al., 2009). Chemical activation is usually carried out at temperature ranging from 400-600°C. The advantages of chemical activation are lower energy cost, shorter activation time, and higher product yield and surface area as compared to the method of physical activation (Ngernyen et al., 2006). However, chemical activation poses problems such as lack of adequate control over porosity development. The activation agents are considered hazardous chemicals and the recovery of these chemical from the products or off gas results in multiple operations. Non-recovery of chemicals not only makes the process uneconomical but also contributes to environmental pollution (Patrick, 1995).

### 2.5.2 Physical activation

Physical activation is the development of porosity by gasification with an oxidizing gas at 700-1100 °C. Commonly used gases are carbon dioxide (Aworn et al., 2009; Bello et al., 2002; Fukuyama et al., 2008; Gonzalez et al., 2009; Ngernyen et al., 2006; Suzuki et al., 2007), steam (Achaw et al., 2008; Arriagada et al., 1994; Aworn et al., 2008; Bouchelta et al., 2008; Gonzalez et al., 2009; Jindaphunphairoth, 2000; Li et al., 2008; Nabais et al., 2008; Tancredi et al., 1996; Sentorun-Shalaby et al., 2006; Zanzi et al., 2001) and air (Ahmad et al., 2007). They can be used singly or in combination. Physical activation can be divided into two steps as follows:

#### 2.5.2.1 Carbonization

Carbonization or pyrolysis is one of the most important steps in the production process of activated carbon. The pyrolysis consists of slow heating of the raw materials at temperature usually below 700°C in the absence of air. The raw materials are carbonized to obtain the char or carbonaceous material, which is activated to yield the highly porous final products (Suzuki et al., 2007). However, the char produced in the pyrolysis step is highly dependent on the initial biomass pyrolyzed. Three steps of the carbonization process are follows:

1. The mass loss is verified by heating the materials up to 200 °C, for moisture content elimination.
2. The mass is greater loss at temperature between 200 and 450 °C at the primary carbonization process. This stage presents a considerably greater weight loss for the raw biomass due to the elimination of volatile matters and tars.
3. The decomposition of a structure with higher stability occurs under the temperature range from 497 to 847 °C. At the temperature above 800 °C, the weight loss is small (less than 10%) with indicates basic structure.

#### 2.5.2.2 Activation

The purposes of activation are to develop the porosity, to create some ordering of the structure and to generate a highly porous solid as the final product. There are usually three stages in the pore development during the activation process: (i) opening of previously inaccessible pores; (ii) creation of new pores by selective activation; and (iii) widening of the existing pores (Li et al., 2008).

Steam and carbon dioxide are commonly used as activating agents. The activating agent 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 stereo-effect, i.e. the steam, carbon dioxide or oxygen molecule needs appropriate space to orientate itself for the reaction which leads to gasification. Thus, the extent of development of porosity and the characteristics of this porosity are a function of:

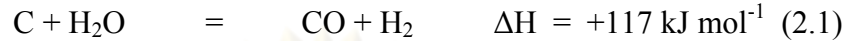
- The structure of the initial carbon
- The presence of catalytic inorganic impurities in the carbon
- The activating agent
- Temperature of gasification
- Pressure of the gas
- Duration of gasification
- Particle size of the carbon

Details of the mechanism by which carbon reacts with steam and carbon dioxide are shown below:

#### 2.5.2.2.1 Activation with steam

Steam is the preferred activation gas because the water molecule has smaller dimension than the carbon dioxide molecule, and consequently the use of steam leads to faster diffusion into the porous network and easier access into the micropores. A faster reaction rate is approximately three times faster than the carbon dioxide reaction at temperature of 800 °C and a pressure of 10 kPa (Patrick, 1995). Gasification with steam produces a more noticeable widening of microporosity to mesoporosity with the increasing effect of activation compared to that obtained by carbon dioxide, which control the competition between the rates of diffusion and gasification reactions (Sentorun-Shalaby et al., 2006). In the steam activation, 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, so creating a wider range of porosities in carbons (Patrick, 1995).

The reactions of carbon with steam to remove carbon atoms from the network within solid carbon are as follows:



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

$$V = \frac{k_1 P_{\text{H}_2\text{O}}}{1 + k_2 P_{\text{H}_2\text{O}} + k_3 P_{\text{H}_2}} \quad (2.2)$$

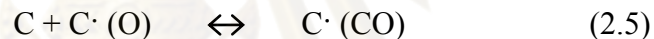
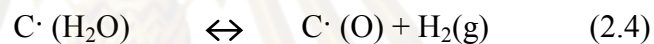
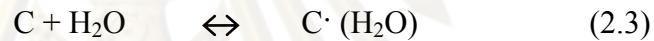
where:

$P_{\text{H}_2\text{O}}$  = the partial pressure of steam

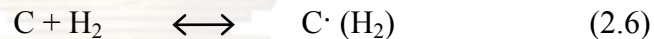
$P_{\text{H}_2}$  = the partial pressure of hydrogen

$k_1, k_2, k_3$  = the experimentally determined rate constants

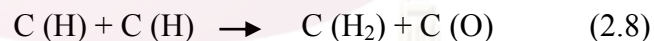
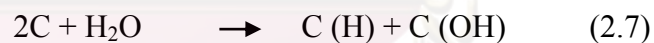
The following reaction scheme is accepted as highly probable:



The steam reaction is product-inhibited; hydrogen is strongly adsorbed on the active centres of the carbon surface and this reduces the reaction rate (Patrick, 1995)

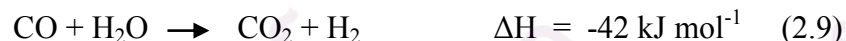


It was assumed that the first step of the reaction is the dissociated adsorption of water molecules according to the scheme:



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

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



Activation with steam is carried out at temperatures from 750 to 950°C with the exclusion of oxygen. These temperatures aggressively attack carbon and decrease the yield by surface burn-off. It is catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metals; the activation catalysts usually employed in

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

#### 2.5.2.2.2 Activation with carbon dioxide

The activation gas is usually carbon dioxide, since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C (Ioannidou et al., 2007).

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



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

$$V = \frac{k_1 P_{\text{CO}_2}}{1 + k_2 P_{\text{CO}} + k_3 P_{\text{CO}_2}} \quad (2.13)$$

where:

$P_{\text{CO}_2}$  = the partial pressures of carbon dioxide

$P_{\text{CO}}$  = the partial pressures of carbon monoxide

$k_1, k_2, k_3$  = the experimentally determined rate constants

Activation with carbon dioxide is inhibited by hydrogen and carbon monoxide. The carbon monoxide acts by increasing the rate of the back reaction [ $\text{C} \cdot (\text{O}) + \text{CO} = \text{C} \cdot + \text{CO}_2$ ]. Rand and Marsh (2006) 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.

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850-1000°C. The activation agent used in technical practice is flue gas which a certain amount of steam is usually added. The catalysts for the reaction with carbon dioxide are carbonates of alkali metals (Patrick, 1995).

The activation by steam is faster than by carbon dioxide due to the mechanisms of gasification reaction that the rate of dissociation and adsorption of intermediate of steam (i.e., H<sub>2</sub>O) to gasifiable active site C\*, ( $C^* + H_2O \leftrightarrow C(O) + H_2$ ), is faster than that of CO<sub>2</sub>, ( $C^* + CO_2 \leftrightarrow C(O) + CO$ ) and CO inhibits further reaction. For further difference between the reaction with steam and carbon dioxide, the larger carbon dioxide molecule compared to steam restricts the ability of carbon dioxide to diffuse through the pores in the carbon and to access the gasifiable sites of inner pore, which results in slower gasification by carbon dioxide than by steam (Fukuyama et al., 2008). Although pore development is dependent on temperature and concentration of reactant gas, the carbon precursor also determines the characteristics of the activated carbon produced.

## 2.6 Effect of Lignocellulosic composition

Essentially, wood is a complex fiber matrix composite material of natural polymers in which the fiber framework consists of crystalline cellulose micro-fibrils, 2-5 nm diameter. The matrix between the micro-fibrils is composed mostly of hemicellulose and lignin which is the strengthening material that reinforces the surrounding cell wall. Typical contents for the biopolymers of hardwoods are: 38-50% cellulose, 23-32% hemicelluloses and 15-25% lignin.

The molecular structures of cellulose, hemicellulose and lignin are shown in Figure 2.1. The micro-fibrils in the cell walls are formed from cellulose chains that are aligned and held together by hydrogen bonding between the hydroxyl groups on the repeating glucose units. Groups of micro-fibrils are connected by amorphous cellulose (about 10-20% of the total cellulose) and hemicelluloses, surrounded by lignin and some hemicelluloses. The spaces between the micro-fibrils are of the order of a few nm, and have the same sizes as the larger micro- and mesopores (Marsh and Rodriguez-Reinoso, 2006).

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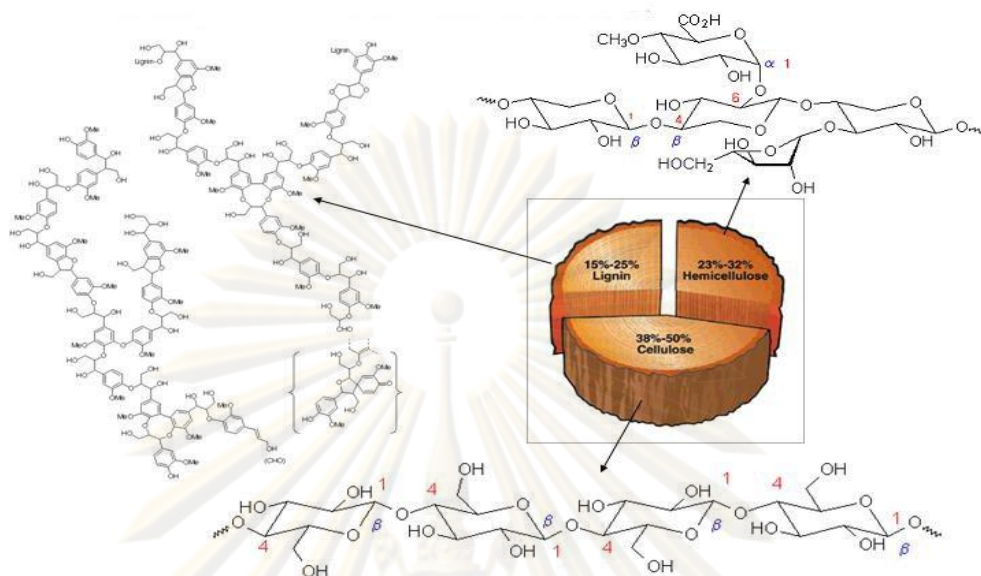


Figure 2.1 Chemical structures of cellulose, lignin and hemicellulose (Whippee et al., 2006)

The production of activated carbons from agricultural by-products suggests that the microstructure is strongly dependent on the original plant texture of the corresponding raw material, which is on the lignin and cellulose content. Hydrolytic lignin and crystalline cellulose were suggested that lignin char has more total pore volume as compared to cellulose char (Gergova et al., 1994). Therefore, the suitable chars can be made from lignocellulosic materials. It was suggested that lignin is the main component responsible for most of the char produced and lignin has a proven ability for sorption (Suhas et al., 2007).

Materials with a greater content of lignin develop activated carbons with microporous structure and higher char yield which in turn produces the highest amount of activated carbons (Gonzalez et al., 2009), while raw materials with a higher content of cellulose yield activated carbon with a predominantly macroporous structure (Ioannidou et al., 2007). The char has more cellulosic content than lignin content that activation rate is higher and it is easier to activate. Moreover, the surface area and the porosity of the material produced with high lignin content (Daud and Ali, 2004). Furthermore, the BET surface area was found to be highest for the raw material with the highest lignin content (Reed and Williams, 2004) whereas the macroporosity was due to cellulose but not lignins and hemicelluloses (Khezami et

al., 2005). A summary of some relevant published data for the properties of chars and activated carbons made from different lignocellulosic precursors is given in Table 2.2.

Table 2.2 Characteristics of biomass and surface area and porosity of the associated activated carbons produced from such biomass

Raw material	Lignin (%)	Cellulose (%)	Yield (%)	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Micropore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Reference
Almond tree	25.0	33.7	26.75	1080	0.568	Gonzalez et al., 2009
Almond shell	24.8	32.5	24.61	601	0.341	Gonzalez et al., 2009
Coir	41-45	36-43	34.40	822	-	Reed and Williams, 2004
Eucalyptus wood	25.9	57.3	-	828	0.360	Ngernyen et al., 2006
Olive stone	32.6	30.8	25.02	813	0.455	Gonzalez et al., 2009
Vetiver roots	33.1	24.5	-	576	0.220	Gaspard et al., 2007
Walnut shell	18.2	40.1	23.96	792	0.442	Gonzalez et al., 2009

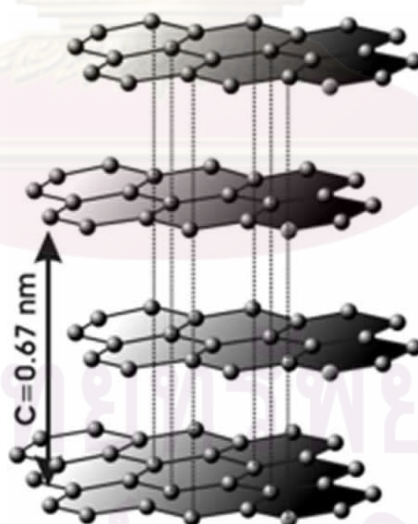


Figure 2.2 Molecular structure of graphite (Patrick, 1995)

## 2.7 Structure of activated carbon

The basic properties of the carbon surface are likely to be due to: (i) functional groups like pyrones, chromenes, ether and carbonyls, that contain less oxygen; (ii) protonated amino groups for nitrogen-rich carbons; (iii) grapheme layers acting as Lewis bases and forming electron donor-acceptor complexes with H<sub>2</sub>O molecules (Gaspard et al., 2007).

The structure of activated carbon is closely approximated by the basic structure unit of pure graphite. The graphite crystal is composed of layers of fused hexagons held by weak van de Waals forces. The layers are held by carbon-carbon bonds (Figure 2.2).

Activated carbon is a disorganized form of graphite, due to impurities and the method of preparation (activation process).

## 2.8 Porosity: definitions

Based on the experiences of adsorption chemistry, total porosity is classified into three groups. The origins and structure of porosities are elaborated upon below. IUPAC classifies porosities as follows:

1. Micropores    width less than 2 nm
2. Mesopores    width between 2 and 50 nm
3. Macropores    width greater than 50 nm

It has also been useful to classify micropores further into ultra- (<0.5 nm width) and super- (1.0-2.0 nm) micropores, these definitions being relevant when considering adsorption behavior (Figure 2.3). Micropores are considered as being about the size of adsorbate molecules and accommodate one, two or perhaps three molecule(s). Mesoporosity is wider and characterized by hysteresis loops during adsorption and desorption at high relative pressures of adsorption. Macroporosity is not much attractive for the surface chemist. It is a transport pore to the interior of particles and considered as external surface. These definitions are not based on direct measurements, nor should they imply rigid size characterization. Rather, it is more meaningful to describe adsorption processes as being microporous and mesoporous in nature. Some activated carbons contain all of these sizes of porosity associated with the botanical composition of the materials (Figure 2.4).

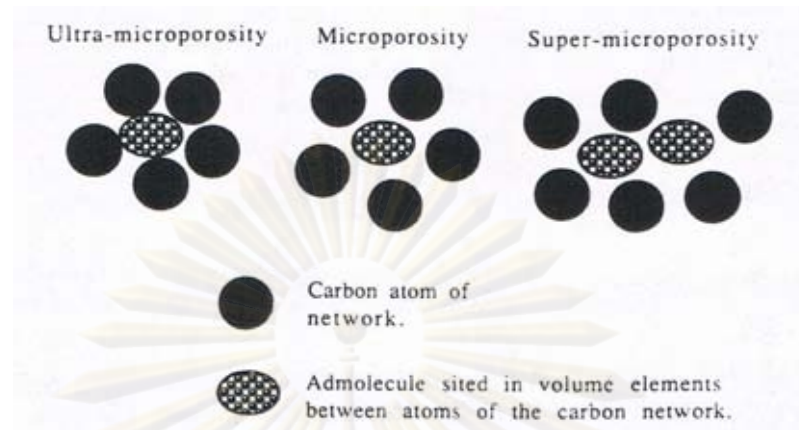


Figure 2.3 Models of sizes of microporosity showing an admolecule of constant size in porosities (volume elements) of increasing size (over-simplified) (Patrick, 1995)

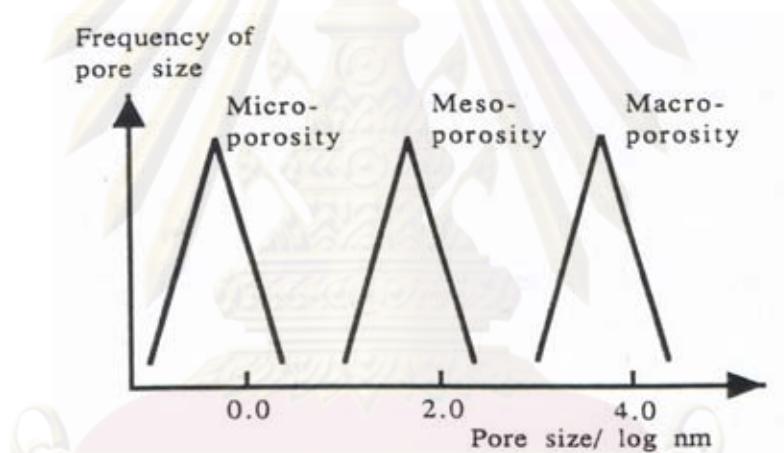


Figure 2.4 Trimodel distribution of porosity found in carbons from natural precursors (Patrick, 1995)

## 2.9 Estimation of the properties of activated carbon

Activated carbon has certain chemical (bulk density, surface area) and physical (ash, moisture content, volatile matter, pore volume, iodine number) properties depending on the basic material source, precursor and activation. These are delineated below.

### 2.9.1 Iodine Number

Many carbons preferentially adsorb small molecules. Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in  $\text{mg g}^{-1}$  (typical range 500-1200  $\text{mg g}^{-1}$ ). It is a measure of the micropore

content of the activated carbon by adsorption of iodine from solution. Iodine number can be up to 1,300 mg g<sup>-1</sup>.

#### 2.9.2 Moisture content

This is the amount of water on the activated carbon under normal condition. High moisture content indicates poor quality and a normal value varies between 1 to 5%.

#### 2.9.3 Ash content

Ash reduces the overall activity of activated carbon and the efficiency of reactivation. This ash consists mostly of calcium salts and metal oxides and comes initially from the basic material. In general, good activated carbon should have low ash content.

#### 2.9.4 Apparent density

Higher density provides greater volume activity and normally indicates better quality activated carbon.

#### 2.9.5 Particle size distribution

The finer the particle size of an activated carbon introduces the better access to the surface area and the faster rate of adsorption kinetics. In vapor phase systems, this needs to be considered against pressure drop which affects energy cost. Careful consideration of particle size distribution can provide significant operating benefits.

#### 2.9.6 Surface area

A range of techniques is available for estimating porosity and surface area. Comparisons are made between results obtained from isotherms and those from other methods. A good activated carbon should have the following characteristics: high porous (microporous structure), large internal surface area, high total surface area (usually, the surface areas of activated carbon are ranging from 500-1400 m<sup>2</sup> g<sup>-1</sup>). Large pore volume is significant for adsorption and is also used to indicate the quality of activated carbon.

## 2.10 Adsorption isotherm

To quantify the adsorption process, extents of adsorption ( $\text{mg g}^{-1}$ ) is related to the equilibrium partial pressure  $p/p^0$  at constant temperature to create the isotherm. Adsorption isotherms are studied to obtain information about the followings:

- Estimates of surface areas
- Estimates of pore volumes in the porosities present, e.g. pore-size of potential energy distributions
- Assessments of the surface chemistry of the adsorbent
- The fundamentals of adsorption process, e.g. the nature of the adsorbed phase

Interpretation of isotherms is not straightforward and this causes considerable debate among surface chemists. Adsorption processes in microporosity are the most difficult to describe accurately. The adsorption process occurring within mesopores are more easily understood. Macroporosity behaves in the same way as an open surface to adsorption, and accounts for less than 1% of the adsorption processes compared to microporous adsorption.

Figure 2.5 sets out the six major classes of isotherm shape obtained from adsorption experiments. Knowledge of adsorption mechanisms in different sizes of porosity is necessary to explain the isotherm shapes.

Type I isotherm is typical of microporous solid in that micropore filling occurs significantly at relatively low partial pressures less than  $0.1 p/p^0$ , the adsorption process being complete at approx.  $0.5 p/p^0$ . Examples include the adsorption of nitrogen on microporous carbon at 77 K and of ammonia on charcoal at 273 K.

Type II isotherm describes physical adsorption of gases by non-porous solids. Monolayer coverage is succeeded by multilayer adsorption at higher  $p/p^0$  values. Type II isotherm can also be obtained from carbons with mixed micro- and mesoporosity.

Type III and Type V isotherms are convex towards the relative pressure axis. These isotherms are characteristic of weak gas-solid interactions. Type III isotherm originates from both non-porous and microporous solids and Type V isotherm is from microporous or mesoporous solids. The weakness of the adsorbent-adsorbate interactions causes the uptakes at low relative pressures to be small; however, once a molecule has become adsorbed at a primary site. The adsorbate-adsorbate forces

promote further adsorption in a cooperative of water molecules on oxides of carbon surfaces. An example is the adsorption of water vapor on graphitized carbon black.

Type IV isotherm possesses a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are associated with mesoporous solids, where capillary condensation occurs.

Type VI isotherm is of surfaces with an extremely homogeneous structure (e.g. pyrolytic graphite) using, for example, argon and methane as adsorbates (but not nitrogen).

The term “surface area” does not describe a carbon unequivocally. Carbons with similar effective surface areas (ESA) can be very different from each other structurally. Furthermore, values obtained using one adsorbate at a certain temperature can differ when other adsorbates at other temperatures are used. When quoting surface areas, it is important to qualify them by including the technique, adsorbate and temperature used.

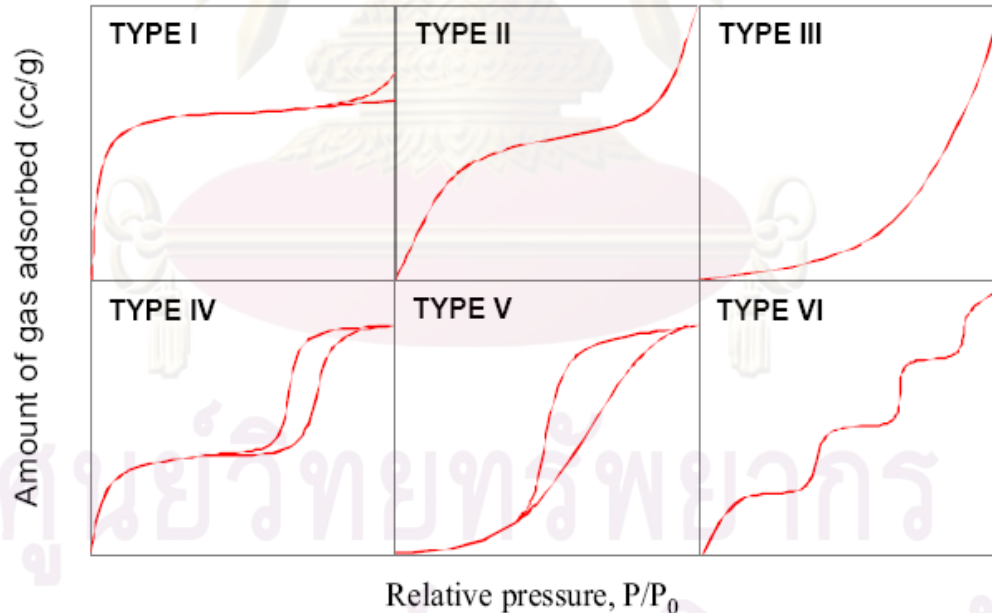


Figure 2.5 Isotherm patterns for the activated carbon (Sing, 1998)

### 2.10.1 Langmuir Isotherm

Langmuir isotherm is based on the following assumptions:

- Only monolayer adsorption can occur;
- Adsorption is localized, with no adsorbate-adsorbate interactions;
- The heat of adsorption is independent of surface coverage, i.e. the adsorbent has a homogeneous surface.

The expression of this isotherm can be described by Equation (2.14)

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (2.14)$$

where;

- $q_e$  = the amount of adsorbed at equilibrium ( $\text{mg g}^{-1}$ )
- $q_m$  = the total number of surface sites per mass of sorbent
- $C_e$  = the remaining concentration of solution after equilibrium ( $\text{mg L}^{-1}$ )
- $b$  = Langmuir constant or capacity factor ( $\text{mg g}^{-1}$ ).

The linear form of equation (2.14) can be written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \quad (2.15)$$

### 2.10.2 Freundlich isotherm

The Freundlich model is a mathematical approach for fitting the experimental data of adjustable parameter to account for the variation in adsorption heat on an energetic heterogeneity of surface with the concentration of adsorbate. The relationship can be described by Equation (2.16):

$$q_e = K_F C_e^{(1/n)} \quad (2.16)$$

where;

- $q_e$  = the amount of adsorbed at equilibrium ( $\text{mg g}^{-1}$ )
- $C_e$  = the remaining concentration of solution after equilibrium ( $\text{mg L}^{-1}$ )
- $K_F$  = Freundlich adsorption constant
- $n$  = Freundlich exponent



The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. The linear form of Equation (2.16) can be written as:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (2.17)$$

The Freundlich isotherm is based on the following assumption: (i) there are many layers (multilayer) of adsorbate on the adsorbent surface; and (ii) adsorbent surfaces are heterogeneous surface. If this isotherm does not match the experimental data, the assumption behind Freundlich isotherm might not hold true. Nevertheless, there is no total capacity term in the Freundlich isotherm equation, so there is no upper limit on adsorption. This condition is less likely to be true for any specific case, and hence, Freundlich isotherm is often used for a specific range of concentration of adsorbate, which is most of the time at the low concentration range.

### 2.11 Applications

Activated carbons concern on many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing. Because of their adsorptive properties, they have a high available area which is presented in their extensive internal pore structure. Such high porosity is a function of both the precursor as well as the scheme of activation.

The chemical nature of activated carbons significantly influences its adsorptive, electrochemical, catalytic, and other properties. Generally speaking, activated carbons with acidic surface chemical properties are favorable for basic gas adsorption such as ammonia while activated carbons with basic surface chemical properties are suitable for acidic gas adsorption such as sulfur dioxide. The uses of the activated carbon produced by agricultural residues are summarized in Table 2.3 (Ioannidou et al., 2006).

Table 2.3 Uses of activated carbons produced by agricultural residues (Ioannidou et al., 2006)

Raw material	Uses
Peanut hulls, rice straw	Treat industrial gas, indoor air (air pollution control) Adsorption of methylene blue (liquid purification) Trace metals
Rice husk, orange peel Palm kernel fibre	Adsorption of acid dyes Removal of ions Removal of Arsenic
Pitch-based carbons Activated carbons membranes Wheat straw	Clean-up of fruits and vegetables Removal of nitrate and pesticides Adsorption of atrazine
Rice husks Jordanian olive stones	Wastewater treatment Groundwater treatment Purification of drinking water Removal of heavy metals Purification of effluent gas streams Removal of mercury vapors Removal of volatile organic compounds Removal of NO <sub>x</sub> and SO <sub>x</sub> Removal of phenols and phenolic compounds

### 2.12 Adsorption of heavy metals

Heavy metals or metallic compounds are used during the manufacturing from industries including pharmaceuticals, chemical, petroleum, mining, nuclear, automobile, etc. Activated carbon is widely used technique for removal of heavy metals such as arsenic (Muniz et al., 2009), cadmium (Fouladi Tajar et al., 2009), chromium (Sarin et al., 2006), copper (Kongsuwan et al., 2009; Patnukao et al., 2008), lead (Acharya et al., 2009; Amarasinghe and Williams, 2007; Boudrahem et al., 2009; Dahiya et al., 2008; Deng et al., 2007; El-Ashtoukhy et al., 2008; Erenturk and Malkoc, 2007; Li and Wang, 2009; Rafatullah et al., 2009), mercury (Ghodbane et al.,

2008; Zhu et al., 2009), 2,4,6-trichlorophenol (Hameed et al., 2008) owing to their highly developed pore structures characterized by large surface areas. However, the chemical nature of their surface often plays a dominating role in their performance as adsorbents, catalysts supports, or catalysts. The chemistry of the surface depends on the presence of heteroatoms, mainly oxygen, which form organic functional groups such as carboxylic acids, lactones, phenols, carbonyls, quinones, aldehydes, ethers, anhydrides and even others (Boudrahem et al., 2009). The behaviors of the adsorption were investigated to examine the effects of initial metal ion concentration, pH, and the enthalpy of adsorption. Langmuir and Freundlich isotherms were used to fit sorption equilibrium data.

### 2.13 Literature review

Most activated carbons have been prepared from agricultural waste because they are abundant and cheap. In principle, the methods for preparing activated carbon can be divided into two categories, i.e. chemical and physical activations. The types of activation and associated properties of raw materials used in the production of activated carbon are represented in Table 2.4. The process for preparation activated carbons are generally two-stage, i.e. carbonization followed by activation. The first stage is to enrich the carbon content and to create an initial porosity where the second, activation, stage helps enhance the pore structure. Table 2.5 presents some carbonization and activation conditions for the production of activated carbons from agricultural residues. Literature demonstrates that ranges of  $N_2$  flow rate, heating rate, were  $100 - 200 \text{ cm}^3 \text{ min}^{-1}$  and  $10 - 25^\circ\text{C min}^{-1}$ , respectively, whilst temperature and time of carbonization were  $300 - 600^\circ\text{C}$  and  $60 - 120 \text{ min}$  and activation process were  $800 - 900^\circ\text{C}$  and  $30 - 120 \text{ min}$ . The surface area, micropore volume and total pore volume of the activated carbon increased with an increasing activation time and temperature with temperature exerting the larger effect. However, the steam activation produced carbons with a narrower and more extensive microporosity, higher BET, and external surface area over the carbon dioxide activation.

Heavy metals are recognized as dangerous contaminants because of their high toxicity, accumulation, and retention in human body. Lead, which is a remarkably toxic and non-biodegradable metal, can be generated by several sources, resulting in

contamination of wastewater and soil. Adsorption has been shown to be one of the most favourable technique for the removal of lead from wastewater. The activated carbon is a unique and effective adsorbent because of their highly developed porosity, large surface area, changeable characteristics of surface chemistry, and high degree of surface reactivity. Table 2.6 summarizes literature reviews of lead adsorption by activated carbon. The percentage removal of lead increases with the increasing in adsorbent dosage and decreases with increasing in initial lead concentration and increasing temperature. The optimal solution pH range for the removal of lead was determined to be around 4 - 6 and the adsorption isotherm often follows the Langmuir type with a maximum adsorption capacity of more than  $10 \text{ mg g}^{-1}$ .



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Table 2.4 Types of activation and associated properties of raw materials used in the activated carbon production

Raw materials	Method of Activation	Activating agent	Properties of activated carbons					References
			Iodine number (mg g <sup>-1</sup> )	Methylene blue number (mg g <sup>-1</sup> )	Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )	Surface area (m <sup>2</sup> g <sup>-1</sup> )	
Almond tree pruning	Physical	CO <sub>2</sub>	-	-	0.568	0.382	1080	Gonzalez et al., 2009
Bagasse and sugar cane	Chemical	H <sub>3</sub> PO <sub>4</sub>	746	-	-	0.258	1132	Castro et al., 2000
Birch	Physical	Steam	-	390	-	-	450	Zanzi et al., 2001
Coconut shell	Physical	Steam	-	-	0.210	-	525	Achaw et al., 2008
	Chemical	NaCl	532	-	-	-	492	Khuysangaim, 2001
	Physical	Steam	-	-	0.931	-	1926	Li et al., 2008
Corncob	Chemical	-	2209	-	-	-	960	Nasser et al., 2001
	Physical	CO <sub>2</sub>	-	-	0.378	0.037	820	Aworn et al., 2009
	Physical	Steam	-	-	0.359	0.037	675	Aworn et al., 2008
Eucalyptus bark	Chemical	H <sub>3</sub> PO <sub>4</sub>	1226	425	-	-	1457	Patnukao et al., 2008
Eucalyptus sawdust	Physical	Steam	-	-	-	-	1190	Tancredi et al., 1996
Eucalyptus wood	Physical	Steam	968	311	-	-	1193	Arriagada et al., 1994
	Physical	Steam	1233	242	-	-	1076	Jindaphunphairoth, 2000
	Physical	CO <sub>2</sub>	1233	-	-	-	-	Bello et al., 2002

Table 2.4 (continued.)

Raw materials	Method of Activation	Activating agent	Properties of activated carbons					References
			Iodine number (mg g <sup>-1</sup> )	Methylene blue number (mg g <sup>-1</sup> )	Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )	Surface area (m <sup>2</sup> g <sup>-1</sup> )	
Eucalyptus wood	Physical	CO <sub>2</sub>	-	-	0.660	-	1491	Ngernyen et al., 2006
Macadamia nut-shell	Physical	Steam	-	-	0.3911	0.094	844	Aworn et al., 2008
Oil palm wood	Physical	Air	-	-	-	0.909	1084	Ahmad et al., 2007
Olive stone	Physical	CO <sub>2</sub>	-	-	0.455	0.100	813	Gonzalez et al., 2009
Plam oil	Physical	Steam	404	162	-	-	284	Suwansangchoto, 1999
Plam shell	Chemical	NaCl	486	-	-	-	386	Khuysangain, 2001
Posidonia oceanica (L.) fibres	Physical	Steam	-	-	0.021	0.118	615	Ncibi et al., 2008
Rice bran	Physical	CO <sub>2</sub>	-	-	0.057	0.075	260	Suzuki et al., 2007
Rubberwood sawdust	Chemical	-	835	255	-	-	822	Kumar et al., 2005
Rubberwood sawdust	Physical	Steam	765	255	-	-	1092	Prakash et al., 2006
Walnut shell	Physical	CO <sub>2</sub>	-	-	0.442	0.082	792	Gonzalez et al., 2009

Table 2.5 Carbonization and activation conditions for the production of activated carbons from agricultural residues

Raw materials	Activating agent	Carbonization				Activation		References
		N <sub>2</sub> Flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Heating rate (°C min <sup>-1</sup> )	Temp (°C)	Time (min)	Temp (°C)	Time (min)	
Almond tree pruning	CO <sub>2</sub>	150	-	600	60	850	30	Gonzalez et al., 2009
Bagasse and sugar cane	H <sub>3</sub> PO <sub>4</sub> (1 : 1.5)	-	-	-	-	500	60	Castro et al., 2000
Coconut shell	Steam (35%)	-	25	325	150	800	120	Achaw et al., 2008
	NaCl (1 : 3)	-	-	-	-	800	60	Khuyasangain, 2001
	Steam	-	50	1000	120	900	120	Li et al., 2008
coffee endocarp	Steam	85	10	600	120	700	45	Nabais et al., 2008
Eucalyptus bark	H <sub>3</sub> PO <sub>4</sub> (1 : 1)	-	-	-	-	500	60	Patnukao et al., 2008
	Steam	-	10	800	120	800	60	Tancredi et al., 1996
Eucalyptus wood	Steam	-	-	450	120	900	270	Arriagada et al., 1994
	Steam	-	-	450	45	900	150	Jindaphunphairoth, 2000
	CO <sub>2</sub>	-	4	870	120	600	30	Bello et al., 2002

Table 2.5 (continued.)

Raw materials	Activating agent	Carbonization				Activation		References
		N <sub>2</sub> Flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Heating rate (°C min <sup>-1</sup> )	Temp (°C)	Time (min)	Temp (°C)	Time (min)	
Eucalyptus wood	CO <sub>2</sub>	100	25	400	60	900	60	Ngernyen et al., 2006
Macadamia nut-shell	Steam	200	20	500	60	800	-	Aworn et al., 2008
Olive kernels	KOH (1 : 4)	-	100-300	270-600	-	900	240	Zabaniotou et al., 2008
	H <sub>2</sub> O-CO <sub>2</sub> mixture.	-	-	800	45	940	180	Zabaniotou et al., 2008
Olive stone	CO <sub>2</sub>	150	-	600	60	850	30	Gonzalez et al., 2009
Plam oil	Steam	-	-	300	30	850	360	Suwansangchuto, 1999
Plam shell	NaCl (1 : 3)	-	-	-	-	800	60	Khuysangain, 2001
Walnut shell	CO <sub>2</sub>	150	-	600	60	850	30	Gonzalez et al., 2009
Waste tyres	Steam	100	-	800	60	900	120	Gonzalez et al., 2006
	CO <sub>2</sub>	100	-	800	60	850	180	Gonzalez et al., 2006
wattle wood	CO <sub>2</sub>	100	25	400	60	800	300	Ngernyen et al., 2006



Table 2.6 Literature reviews on the adsorption of lead by activated carbon

Adsorbent	Condition			Efficiency (%)	Isotherm	References	
	pH	Initial lead concentration (mg L <sup>-1</sup> )	Adsorbent (g L <sup>-1</sup> )				Time (hr)
Cladophora fascicularis	5	100	2.5	6	90	Langmuir: $q_m = 198.5 \text{ mg g}^{-1}$ , $b = 0.0357 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 37.46 \text{ mg g}^{-1}$ , $1/n = 3.621$	Deng et al., 2007
Coffee residue	5.8	10	63 mg g <sup>-1</sup>	-	-	Langmuir: $q_m = 63.291 \text{ mg g}^{-1}$ , $b = 0.396 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 27.495 \text{ mg g}^{-1}$ , $1/n = 0.244$ Temkin: $q_e = 13.123 \text{ mg g}^{-1}$ , $b = 4.1334$	Boudrahem et al., 2009
Crab and Arca shell	5.5	100	2.5	24	99.1	Langmuir: $q_m = 33.89, 30.39 \text{ mg g}^{-1}$ , $b = 0.056, 0.069 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 8.194, 1.848 \text{ mg g}^{-1}$ , $1/n = 0.246, 0.353$ Lagergren: $q_e = 26.63, 18.63 \text{ mg g}^{-1}$ , $K_L = 0.02, 0.013$	Dahiya et al., 2008
meranti sawdust	6	100	5	2	-	Langmuir: $q_m = 34.246 \text{ mg g}^{-1}$ , $b = 0.016 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 1.504 \text{ mg g}^{-1}$ , $1/n = 1.046$ Dubinin–Radushkevich: $C_m = 0.410 \text{ mg g}^{-1}$ , $R^2 = 0.998$	Rafatullah et al., 2009

Table 2.6 (continued)

Adsorbent	Condition			Efficiency (%)	Isotherm	References	
	pH	Initial lead concentration (mg L <sup>-1</sup> )	Adsorbent (g L <sup>-1</sup> )				Time (hr)
Pomegranate peel	5.6	-	-	2	-	Langmuir: $q_m = 17.637 \text{ mg g}^{-1}$ , $b = 0.260 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 8.422 \text{ mg g}^{-1}$ , $1/n = 0.463$ Temkin: $q_e = 9.39 \text{ mg g}^{-1}$ , $b = 3.753$	El-Ashtoukhy et al., 2008
Spartina alterniflora	5-6	46.9-69.8	0.5	0.33	-	Langmuir: $q_m = 99.5 \text{ mg g}^{-1}$ , $b = 0.222 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 31.57 \text{ mg g}^{-1}$ , $1/n = 0.270$	Li and Wang, 2009
Tea waste	5-6	-	0.25-1.5	-	37-94	Langmuir: $q_m = 65 \text{ mg g}^{-1}$ , $b = 0.0494 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 9.65 \text{ mg g}^{-1}$ , $1/n = 0.3885$	Amarasinghe and Williams, 2007
Tamarind wood	-	10-50	-	-	99	Langmuir: $q_m = 43.859 \text{ mg g}^{-1}$ , $b = 0.274 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 9.321 \text{ mg g}^{-1}$ , $1/n = 0.668$	Acharya et al., 2009
Viscum album L.	5	50	0.8	1.5	99	Langmuir: $q_m = 769.23 \text{ mg g}^{-1}$ , $b = 0.034 \text{ (mg/L)}^{-1}$ Freundlich: $K_F = 101.86 \text{ mg g}^{-1}$ , $1/n = 0.3748$ Temkin: $B = 138.24$ $A = 0.653 \text{ L mg}^{-1}$ Harkins-Jura: $A = 50,000$ , $B = 2.0$	Erenturk and Malkoc, 2007

# CHAPTER III

## RESEARCH METHODOLOGY

### 3.1 Materials

#### 3.1.1 Chemical reagents

- Deionized water (DI water)
- Hydrochloric acid (HCl)
- Iodine ( $I_2$ )
- Lead nitrate ( $Pb(NO_3)_2$ )
- Potassium iodine (KI)
- Potassium iodate ( $KIO_3$ )
- Potassium phosphate ( $KH_2PO_4$ )
- Sodium carbonate ( $Na_2CO_3$ )
- Sodium thiosulfate ( $Na_2S_2O_3 \cdot 5H_2O$ )
- Sodium phosphate ( $Na_2HPO_4$ )
- Starch solution

#### 3.1.2 Equipments

- Analytical Balance (2 digits), Sartorius, BP 3100S
- Atomic Absorption Spectrophotometer (AA), Varian, AA 280 FS
- Digital Balance (4 digits), Sartorius, BP 2215
- Desiccators
- CHNS/O Analyzer, Perkin Elmer PE2400 Series II
- Conical tube
- Filter paper No. 42, Whatman
- Flow Meter
- Fourier Transform Infrared Spectrometer (FT-IR), Perkin Elmer, Spectrum One
- Gases regulator

- Horizontal tubular furnace
- Micropipette
- Muffle furnace: type ESF 12/23 (0-1200 °C), Carbolite, England.
- Oven, WTB binder, FD115 (E2)
- Rotary Shaker, GFL, 3017
- Scanning Electron Microscopy (SEM), JEOL, JSM-5410LV
- Surface area analyzer, Quantachrome, Autosorb-1MP
- X-ray Diffractometer (XRD), Bruker, D8- Discover

### 3.2 Preparation of activated carbon

#### 3.2.1 Furnace system

The schematic of experimental setup is shown in Fig. 3.1. The furnace system consists of horizontal tubular furnace (8), tubular reactor (6), gas cylinder (N<sub>2</sub>, air and CO<sub>2</sub>) (1, 2, 3) and steam generator (4, 5). The horizontal tubular reactor was made of SS304 steel with a minimum volume of 150cc. This tubular reactor had the flange with an outside diameter of 40 mm and internal diameter of 35 mm and was placed in the horizontal tubular furnace. The horizontal tubular furnace could be heated up to 1100°C with a fixed heating rate of 10°C min<sup>-1</sup>. The steam was generated by pumping DI water with peristaltic pump through the heater at 140°C and carried into the tubular reactor by N<sub>2</sub> carrier gas through the piping network made of stainless steel (SS316L size 1/4").

#### 3.2.2 Preparation of Eucalyptus bark

1. Wash the eucalyptus bark, from Advance Agro Public Co., Ltd., Prachinburi province, Thailand, with DI water
2. Dry the eucalyptus bark at 105°C for 4 hours to remove excess water
3. Crush and sieve pass through out mesh number 20 (0.853 mm)
4. Store the eucalyptus bark in closed bottle to protect it from moisture
5. Analyze the proximate and ultimate of the eucalyptus bark

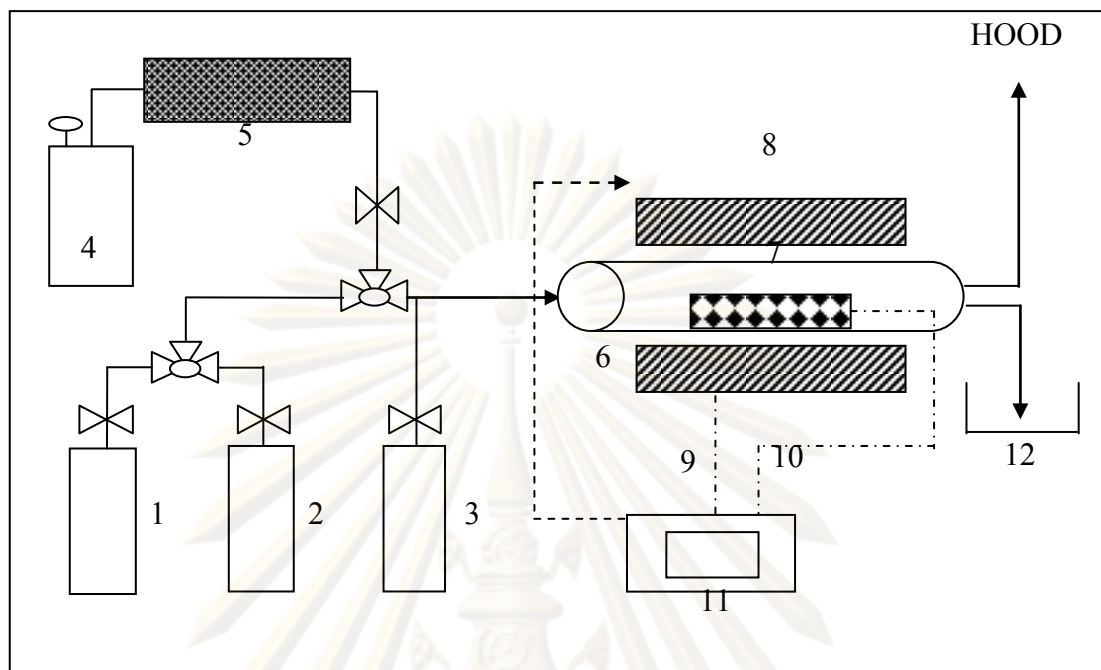


Figure 3.1 Schematic diagram of the experimental set up: (1) nitrogen gas cylinder; (2) air cylinder; (3) carbon dioxide cylinder; (4) peristaltic pump; (5) heater; (6) tubular reactor; (7) sample; (8) tubular furnace; (9) furnace thermocouple; (10) sample thermocouple; (11) temperature controller; (12) beaker (liquid product collectors)

### 3.2.3 Preparation of activated carbon

#### 3.2.3.1 Determination of the optimal condition for carbonization

1. Weigh 50 g of eucalyptus bark (from Section 3.2.2), place in the middle of tubular reactor and put the reactor in the horizontal tubular furnace
2. Carbonize the eucalyptus bark in muffle furnace at various temperatures (450-600°C), and various times (30-120 minutes)
3. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle
4. Determine optimal carbonization condition by proximate analysis

#### 3.2.3.2 Determination of the optimal condition for activation

1. Weigh 50 g of charcoal (from 3.2.4.1), place in the middle of reactor and put the reactor in the horizontal tubular furnace

2. Carbonize under the flow of N<sub>2</sub> gas at 200 cm<sup>3</sup> min<sup>-1</sup>, the heating rate is controlled at 10°C min<sup>-1</sup> starting from room temperature (30°C) to final temperature of 850, 900, 950°C, respectively

3. Activate by switching N<sub>2</sub> to steam or CO<sub>2</sub> at various times 60, 90 and 120, and then, cool down by switching the gas flow to N<sub>2</sub>.

4. Analyze activated carbon characteristics by proximate and ultimate analysis, iodine number, and BET surface area

### 3.2.4 Analysis of activated carbon properties

1. Ash content: determined by standard method ASTM D 2866-94 (detail in Appendix A.1).

2. Apparent (bulk) density: calculated as the ratio between weight and volume of packed dry material (detail in Appendix A.2).

3. Chemical analysis of wood charcoal: determined according to the standard method ASTM D 1762-84. This method covers the determination of moisture, volatile matter, and ash in charcoal made from wood (detail in Appendix A.3).

4. Fourier Transform Infrared Spectrometer (FT-IR): determined functional groups attached in activated carbon.

5. Iodine number: determined according to the standard method ASTM D 4607-94 (detail in Appendix A.4).

6. Moisture content of activated carbon: determined according to the standard method ASTM D 2867-95 (details in Appendix A.5).

7. Surface area: calculated from adsorption isotherms using the method of Brunauer, Emmet and Teller (BET method) and see details in Appendix A.6.

8. The surface morphology of activated carbon: visualized via scanning electron microscopy (SEM), and the corresponding SEM micrographs were obtained using a XL 30 ESEM FEG scanning electron microscope.

9. Ultimate analysis of eucalyptus bark: performed by CHNS/O analyzer (Perkin Elmer PE2400 Series II), using gaseous products feed by pyrolysis in high purity oxygen and were chromatographically detected with a thermal conductivity detector. The proximate analysis was developed following ASTM standards for chemical analysis of wood charcoal (ASTM D 1762-84).

10. X-ray diffraction (XRD) patterns: obtain in a X-ray Diffraction Spectroscopy using Cu K $\alpha$  radiation ( $\lambda=0.154056$  nm), with a step size of  $0.004^\circ$  and a step time of 1.5 s.

11. Yield of activated carbon: the yield is defined as the ratio of the weight of the resultant activated carbon to that of the original eucalyptus bark with both weight on a dry basis, i.e.

$$\% \text{Yield} = \frac{W_1}{W_0} \times 100 \quad (3.2)$$

where  $W_0$  is the original mass of the precursor on a dry basis and  $W_1$  is the mass of the carbon after activation, washing and drying

### 3.3 Sorption studies

#### 3.3.1 Preparation of synthetic wastewater

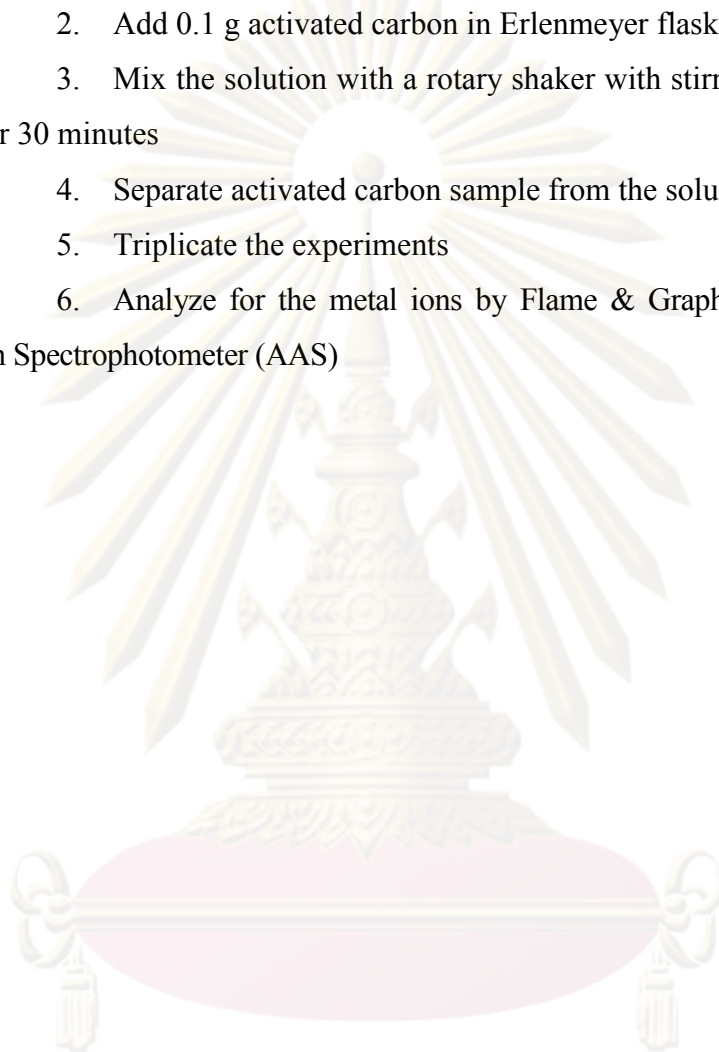
1. Pipette the standard solution of  $\text{Pb}(\text{NO}_3)_2$  at concentration of  $1000 \text{ mg L}^{-1}$
2. Dilute with deionized water until the concentrations of solution are 10, 20, 30, 40 and  $50 \text{ mg L}^{-1}$
3. Stock in polyethylene bottles

#### 3.3.2 Effect of pH for adsorption

1. Adjust pH of synthetic wastewater with NaOH or  $\text{HNO}_3$  to 1, 2, 3, 4 and 5
2. Add  $50 \text{ mg L}^{-1}$  synthetic wastewater concentration of 10, 20, 30, 40 and  $50 \text{ mg L}^{-1}$  to 150 ml Erlenmeyer flask
3. Add activated carbon 0.1 g in Erlenmeyer flask
4. Mix the solution with a rotary shaker with stirring rate of 200 rpm at  $30^\circ\text{C}$  for 120 minutes
5. Separate activated carbon from the solution after shake
6. Triplicate the experiments
7. Analyze for the metal ions by Flame & Graphite Furnace Atomic Absorption Spectrophotometer (AAS)

### 3.3.3 Determination of adsorption isotherm

1. Add 50 ml synthetic wastewater concentration of 10, 15, 20, 25, 30, 40 and 50 mg L<sup>-1</sup> at pH 4 to 150 ml Erlenmeyer flask
2. Add 0.1 g activated carbon in Erlenmeyer flask.
3. Mix the solution with a rotary shaker with stirring rate of 200 rpm at 30°C for 30 minutes
4. Separate activated carbon sample from the solution after shake
5. Triplicate the experiments
6. Analyze for the metal ions by Flame & Graphite Furnace Atomic Absorption Spectrophotometer (AAS)



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## CHAPTER IV

### Results and Discussion

#### 4.1 Characterization of eucalyptus bark

Eucalyptus bark, the precursor material in this experiment, was procured from the actual pulp mill in Prachinburi province. The eucalyptus bark was repeatedly washed with DI water in order to remove dust and other inorganic impurities, then oven dried for 4 h at 105 °C to remove the moisture content. The dried biomass was crushed and sieved through the mesh number 20 (approx. 0.853 mm). The pictures of eucalyptus bark before and after crushed and sieved, and activated carbon from eucalyptus bark are shown in Figure 4.1 (a) – (c). Table 4.1 summarizes properties of the eucalyptus bark which revealed that eucalyptus bark had a relatively high carbon content (more than 40%) and low contents of nitrogen (0.63%) and ash (7.9%). As mentioned in the Chapter 2, carbon content or fixed carbon is one of the main properties to produce activated carbon through gasification and pyrolysis processes. This means that eucalyptus bark which was proved to present high carbon content (40%) could be suggested to be a potential material in being converted to activated carbon. This level of carbon content is also comparable to that in other types of raw materials such as almond tree (51.3%), corncob (49.0%), and olive stone (44.8%) (Aworn et al., 2009; Gonzalez et al., 2009).



Figure 4.1 (a) Eucalyptus bark before crushed and sieved (b) Eucalyptus bark after crushed and sieved (c) activated carbon from Eucalyptus bark

Table 4.1 Properties of Eucalyptus bark

Ultimate analysis	(wt %)
C	42.60
H	4.80
N	0.63
O (balance)	51.97
Proximate analysis	(wt %)
Moisture	6.7
Volatiles	68.6
Ash	7.9
Fixed carbon	16.8

#### 4.2 Optimal carbonization condition

Activated carbons were produced from Eucalyptus bark through the process of carbonization followed by steam and carbon dioxide activations. During the carbonization process, eucalyptus bark was carbonized in the absence of air at various temperatures (450, 500, 550 and 600°C) and various times (30, 45, 60, 90 and 120 minutes). The results of these experiments are shown on below. (Raw data are given in Table B.1 in Appendix B).

##### 4.2.1 Yield

The yield of charcoal can be defined as the ratio of the mass of charcoal upon the mass of raw material used. The %yield of charcoal is calculated from:

$$\%Yield = \frac{W_1}{W_0} \times 100 \quad (4.1)$$

where  $W_0$  is the original mass of precursor on a dry basis and  $W_1$  the mass of the charcoal after carbonization. The attainable yields at various activation conditions are given in Figure 4.2.

At a constant holding time, as the carbonization temperature increased from 450 to 600°C, the yield of charcoal decreased. This was attributed to the removal of volatile matters and tars resulting from the decomposition of major compounds.

Above 550°C, the weight loss was small which indicated the basic structure of the char with no or only slight volatile content.

At constant carbonization temperature, as the hold time increased from 30 to 120 minutes, the percentage yield decreased continuously. Higher temperature obtained by prolonging carbonizing period caused the elimination of tars and other hydrocarbons (including volatile organic compounds) from porous structure in the form of liquid and gaseous products.

#### 4.2.2 Fixed carbon

Figure 4.3 demonstrates that percent of fixed carbon of the charcoal continuously increased with an increase in carbonization temperature and time. This could potentially be due to the removal of volatile matter and moisture from eucalyptus bark. The fixed carbon of charcoal is calculated from:

$$\text{Fixed carbon (\%)} = 100 - (\text{ash (\%)} + \text{volatile matter (\%)} + \text{moisture (\%)}) \quad (4.2)$$

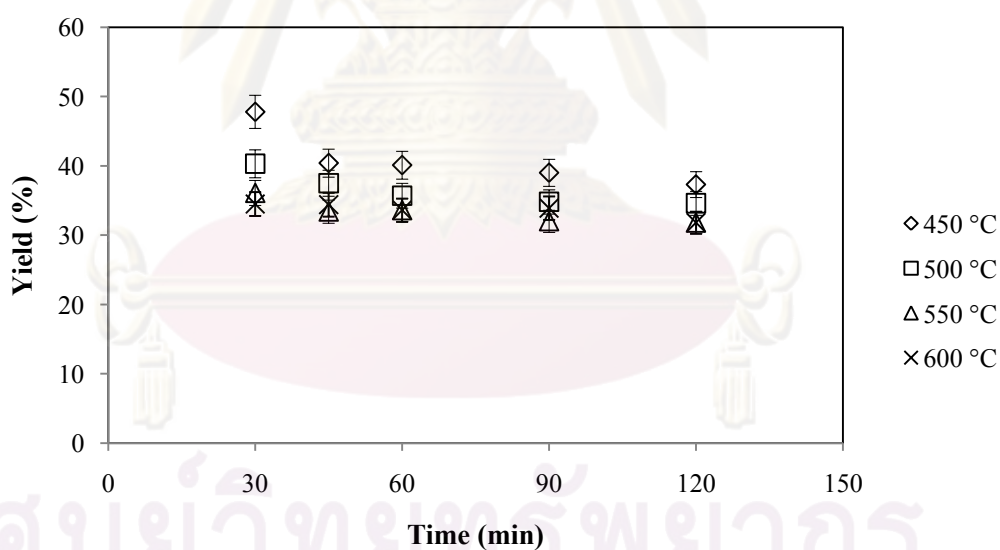


Figure 4.2 Effect of carbonization temperature and time on yield of charcoal

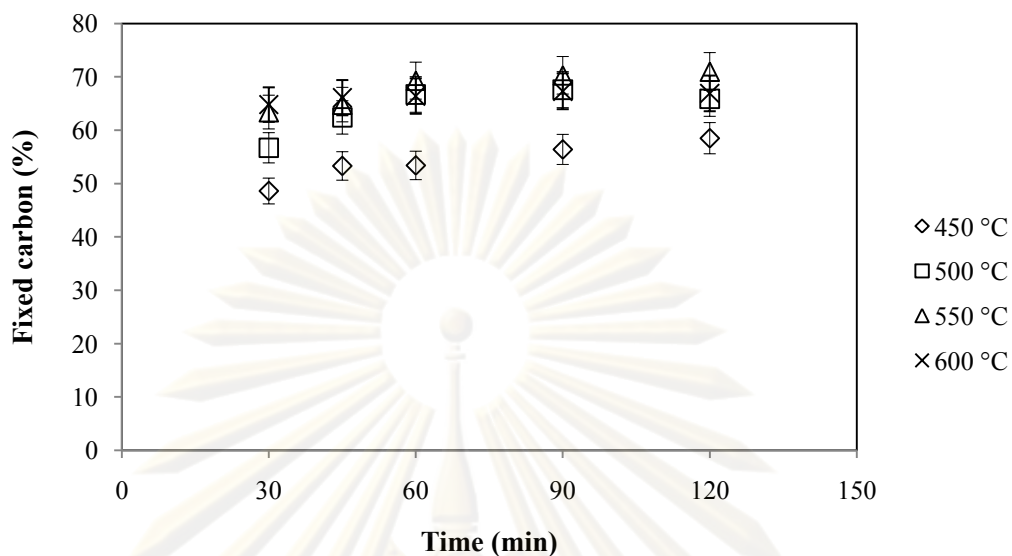


Figure 4.3 Effect of carbonization temperature and time on fixed carbon of charcoal

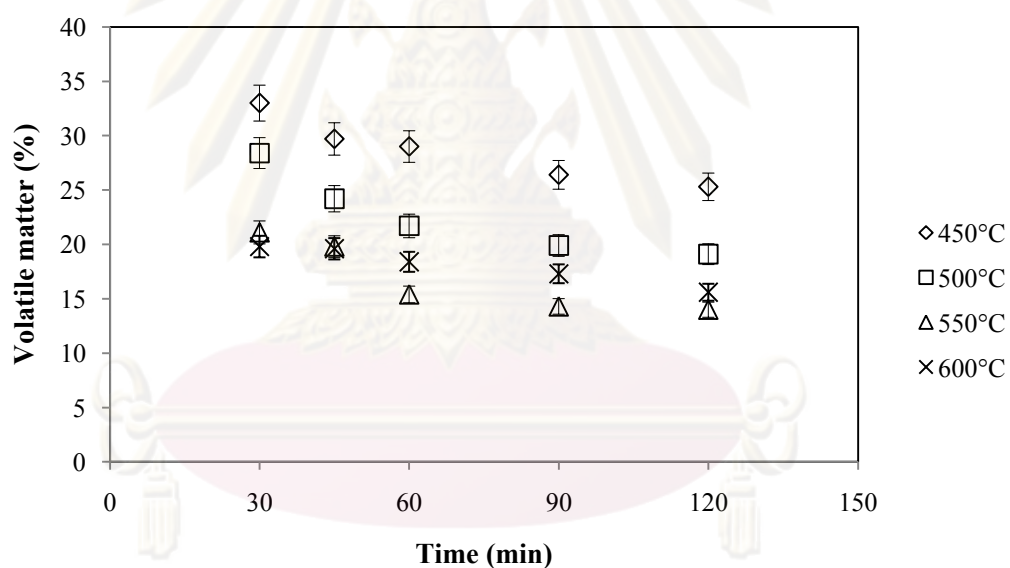


Figure 4.4 Effect of carbonization temperature and time on volatile matter of charcoal

#### 4.2.3 Volatile matter

Figure 4.4 shows the effect of the carbonization temperature and carbonization time on the volatile matter of charcoal. Higher carbonization temperature (450 to 600°C) caused a decrease in the amount of volatile matter due to devolatilization and thermal degradation of extractives as well as high-molecular weight hydrocarbons.

#### 4.2.4 Ash content

The ash content was estimated from the mass of the residue remained after combustion of the samples in air. Figure 4.5 demonstrates that ash content of charcoal increase with increasing carbonization temperature and time due to the changes in the weight of compounds resided in the matrix of carbon.

At high temperature, the ash content of charcoal increased with temperature. This was ascribed to the faster removal rate of other volatile components than the uncombustible constituents like silica. The same reason applied to the effect of holding time, i.e. when the holding time increased from 30 to 120 minutes, % ash content slightly increased.

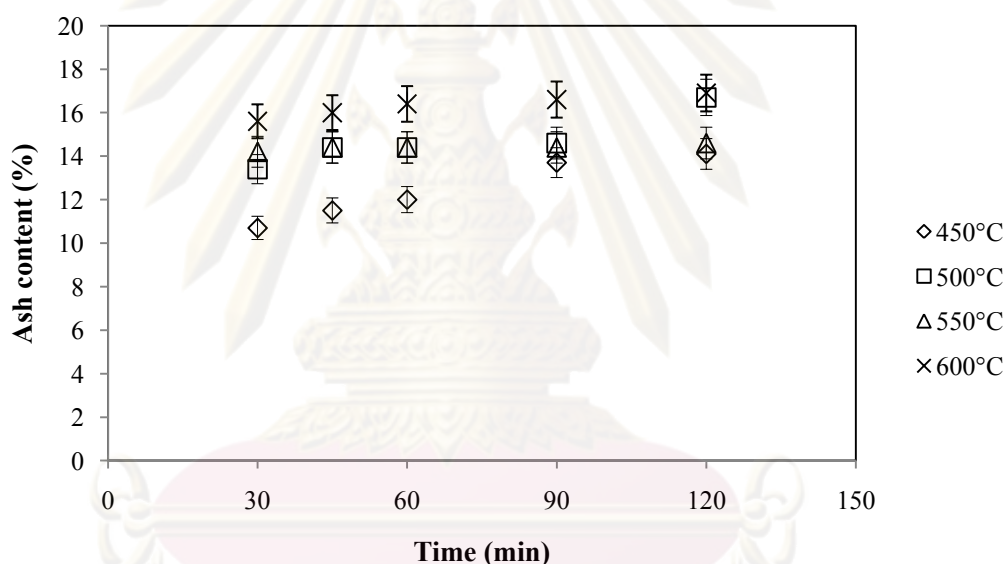


Figure 4.5 Effect of carbonization temperature and time on ash content of charcoal

#### 4.2.5 Concluding remarks on Carbonization

Carbonization is one of the most important steps in the production process of activated carbon because the initial porous structure is formed and activation develops this structure further. Jindaphunphairoth (2000) and Aworn et al. (2009) showed that suitable charcoal for the activation should have volatile matter in the range of 20-25%. It was possible that the excess residual volatile in charcoal obstructed the activating agent activity in forming porous structure. On the other hand, a much too low residual volatile caused the activating agent to react with the char structure resulting in the formation of mesopore. From the above results, the optimal

carbonization condition for the production of eucalyptus bark activated carbon was 500°C at 45 minutes. With these conditions, the obtained char contained a proper content of volatile matter (24.2%), high content of fixed carbon (62.4%), yield (37.5%), bulk density 0.41 g cm<sup>-3</sup>, iodine number 169 mg g<sup>-1</sup> and surface area 179 m<sup>2</sup> g<sup>-1</sup> (Table 4.2). The low surface area charcoal might be the results from the blockage of the structure by residual tar. Therefore, the charcoal must be activated by activating agent to increase the porosity.

Table 4.2 Properties of charcoal (Carbonized product)

Ultimate analysis (wt %)	
C	53.01
H	1.55
N	0.54
O,S (balance)	44.90
Proximate analysis (wt %)	
Moisture	1.4
Volatiles	24.2
Ash	12.0
Fixed carbon	62.4
Yield (wt %)	37.5
Bulk density (g cm <sup>-3</sup> )	0.41
Iodine number (mg g <sup>-1</sup> )	169
Surface area (m <sup>2</sup> g <sup>-1</sup> )	179

### 4.3 Optimal activation condition by steam

The activation step is designed to develop the porosity in the material to generate a highly porous solid as the final product due to the removal of some components, e.g. tar like matter, and disorganized carbon deposited in pore. The effect of activation temperature and time were carried out at various temperatures: 850, 900 and 950°C and various times: 60, 90 and 120 minutes using steam as an

activating agent. The property of activated carbon obtained from the experiment is shown in Table B.2 in Appendix B.

#### **4.3.1 Yield**

The yield of activated carbon is defined as the ratio of mass of activated carbon produced and the mass of charcoal used. Figure 4.6 shows the effect of activation temperature and time on yield of activated carbon.

The temperature was shown to markedly affect the yield. At higher temperatures, the yield of activated carbon decreased due to the removal of volatile components, e.g. tar like matter, and disorganized carbon deposited in pore. The experiments at 950°C resulted in a low yield of activated carbon due to intensified gasification.

Increasing activation time slightly decreased the yield. This was expected as increasing times of activation also favored the release of volatiles, similar circumstance to the effect of increase in temperature.

#### **4.3.2 Ash content**

In general, ash content in activated carbon is not desirable and is considered an impurity. Figure 4.7 demonstrates that % ash content of activated carbon increased with increasing activation temperature and activation time. This is due to an increase in the gasification at higher activation temperature which led to a more intensified removal of organic contaminants in the eucalyptus bark.

#### **4.3.3 Bulk density**

Figure 4.8 shows that bulk density of activated carbon slightly decreased with increasing activation temperature. This could potentially be due to the removal of volatile matter and tar deposited in pore which occurred better at higher activation temperature so the activating agent easily diffused to develop of porosity.

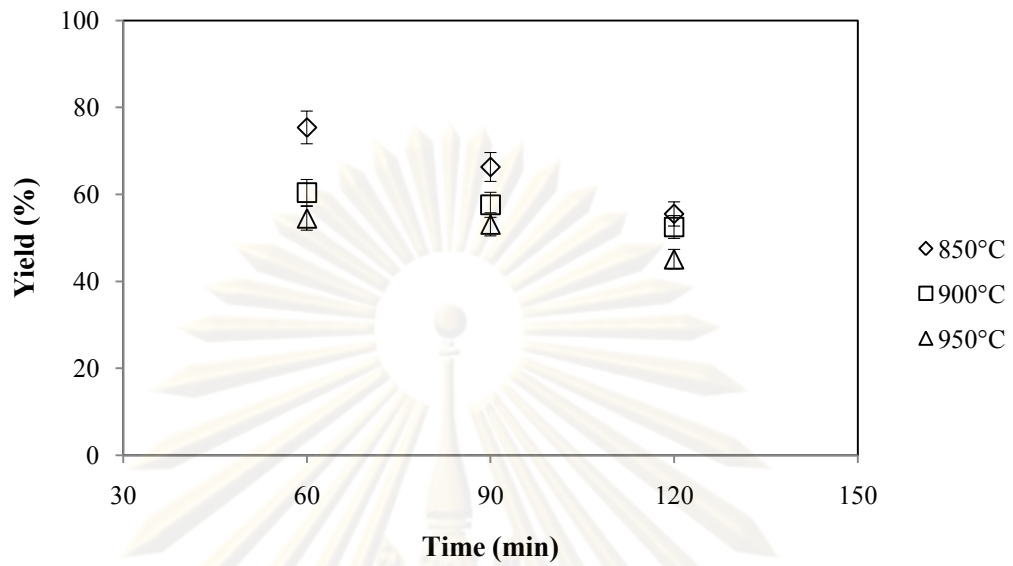


Figure 4.6 Effect of activation temperature and time on yield of steam activated carbon

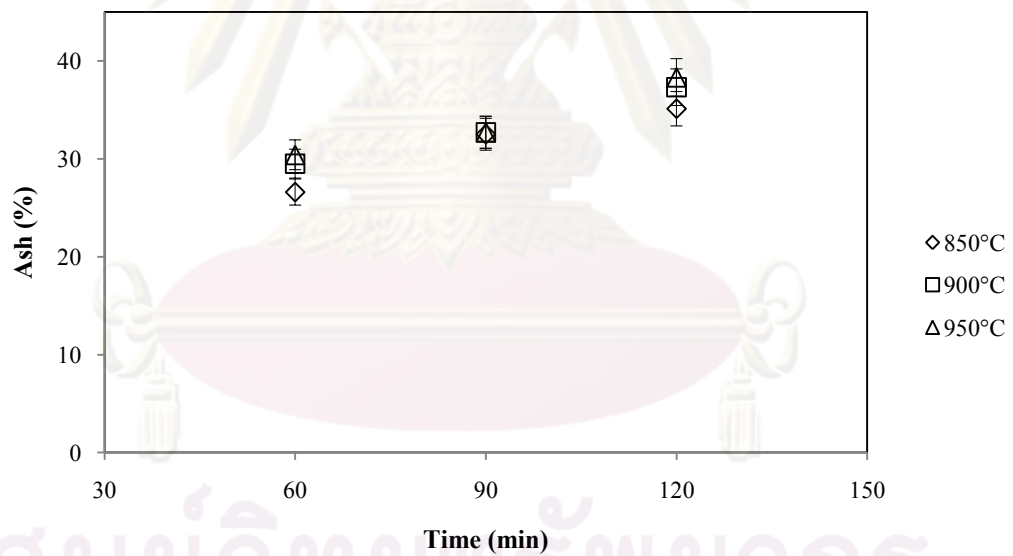


Figure 4.7 Effect of activation temperature and time on ash content of steam activated carbon

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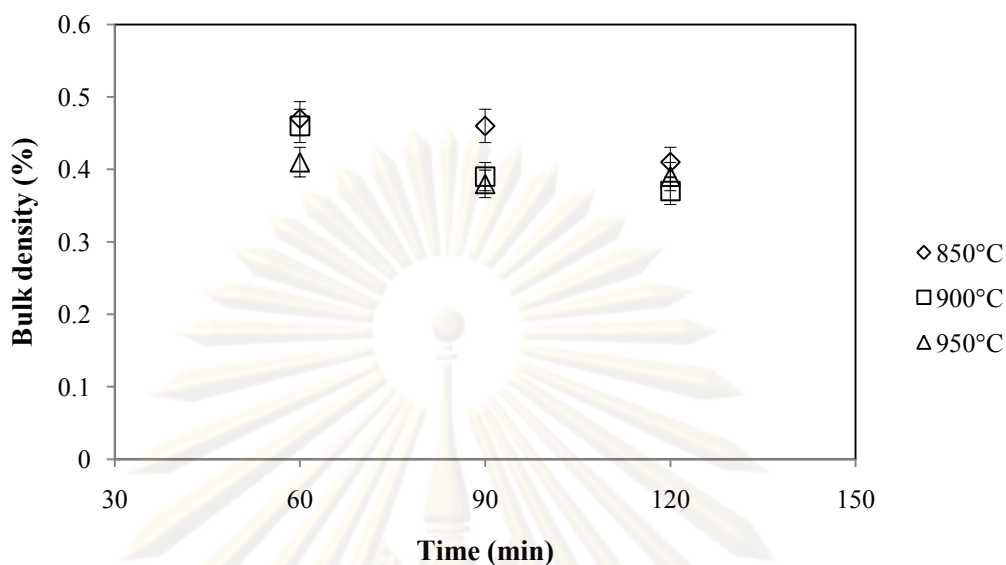


Figure 4.8 Effect of activation temperature and time on bulk density of steam activated carbon

#### 4.3.4 Iodine number

When the steam as the activating agent comes in contact with the charcoal, it reacts both with the exterior and the interior of the charcoal, the result will be the enlargement of opened micropores and the opening up of closed micropores. With regard to effect of activation temperature, the resulting iodine number was in the range of 300-700 mg g<sup>-1</sup>. The iodine number increased gradually with activation temperature (850-950°C). The results demonstrate that the volatile matter and tar in the pore structure was more rapidly removed allowing the activating agent to better enter the charcoal structure resulting in a larger surface area which corresponded to a higher level of iodine number (see Figure 4.9).

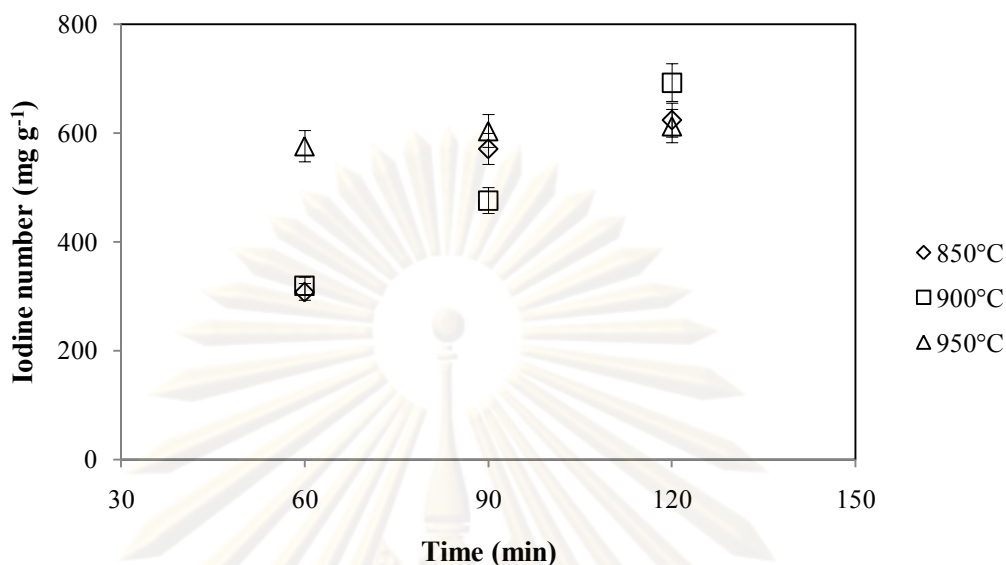


Figure 4.9 Effect of activation temperature and time on iodine number of steam activated carbon

The effect of activation time on iodine number at various temperatures is shown in Figure 4.9. Increasing activation time from 60 to 120 minutes led to a rapid increase in iodine number when the activation temperature was 850°C and 900°C. The highest iodine number of 693 mg g<sup>-1</sup> was obtained from the activation at 120 minutes and 900°C, which indicated the development of micropores. Increasing temperature upto 950°C saw only a slight increase in iodine number. It was possible that the formation of microporosity was counteracted by the destruction of pore due to the high gasification rate at this high temperature.

#### 4.3.5 Surface area and pore volume

The surface area can be represented by several parameters, and one of those is iodine number. BET surface area and pore volume were only tested for those samples with best iodine number profile. The specific surface area (up to 794 m<sup>2</sup> g<sup>-1</sup>) was obtained from the BET calculation, where the shape of the adsorption-desorption of nitrogen isotherms as demonstrated in Figure 4.10 indicated that the product was Type I isotherm according to IUPAC classification. This shape is the characteristics of the microporous structure, as there is a large amount of nitrogen adsorbed at low relative pressure and an increase in the adsorbed nitrogen at higher relative pressure

revealed the mesoporous structure (corresponding well to the results display in Table 4.3 where 84% was micropore and 16% mesopore). This is an indication of uniform microporosity development during the activation.

The optimal condition for production of activated carbon is indicated using the following parameters: i.e. iodine number, yield and bulk density. The best activated carbon was produced by steam activation at 900 °C 120 minutes, where the obtained activated carbon contained a proper content of carbon (64.80%) and ash (37.3%) and with the following properties: yield (52.5 %), bulk density 0.37 g cm<sup>-3</sup>, iodine number 693 mg g<sup>-1</sup> and surface area 794 m<sup>2</sup> g<sup>-1</sup> (Table 4.3). The properties of activated carbon are compared with the charcoal as illustrated in Tables 4.2 and 4.3. The carbon content from activated carbon was higher than the charcoal (53.01%) owing to a decrease in amount of volatile matter and an increase in fixed carbon at higher temperature.

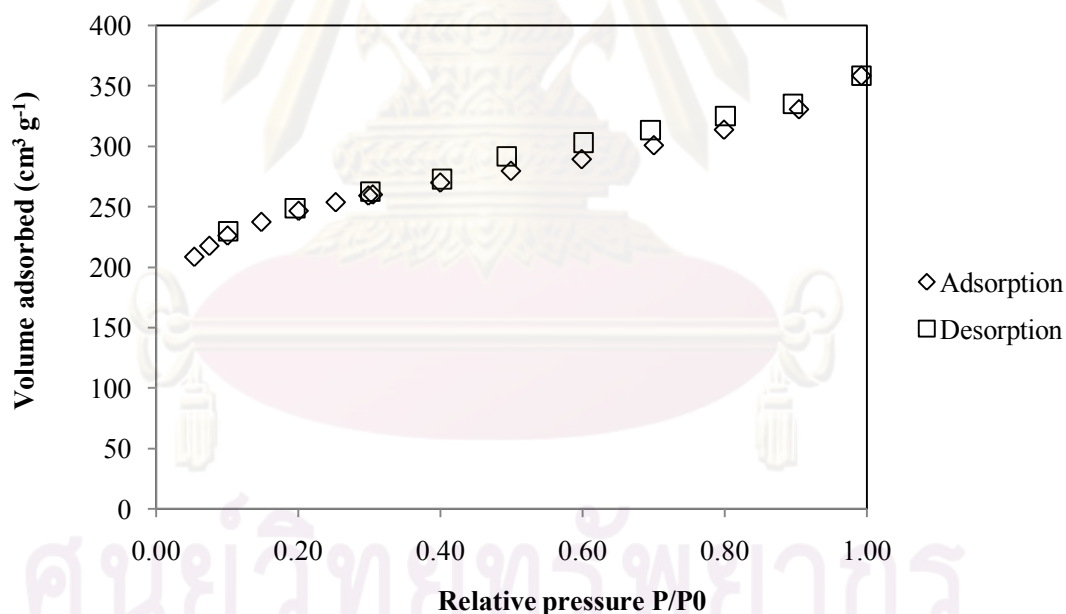


Figure 4.10 N<sub>2</sub> adsorption and desorption isotherms at 77K on steam activated carbon

Table 4.3 Properties of activated carbon from steam activation

Properties	Value
<i>Ultimate analysis (wt %)</i>	
C	64.80
H	0.69
N	0.19
O,S (balance)	34.30
<i>Physical properties</i>	
Yield (wt %)	52.5
Ash (wt %)	37.3
Bulk density (g cm <sup>-3</sup> )	0.37
Iodine number (mg g <sup>-1</sup> )	693±63
BET Surface area (m <sup>2</sup> g <sup>-1</sup> )	794
- Micropore (%)	84
- Mesopore (%)	16
- Average pore diameter (Å)	27.95
- Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.555

#### 4.3.6 Optimal activation condition by steam

Experimental results demonstrate that the optimum activation condition for the highest iodine number was 900°C for 120 minutes. The activated carbon from this work is compared with the others with the same raw materials (Eucalyptus) as illustrated in Table 4.4. The overall yield on dry basis from this work was 52.5% which was higher than the reported values such as *Eucalyptus camaldulensis* Dehn bark (30.5% and 26%) (Thongton, 2008, Patnukao et al., 2008 respectively), *Eucalyptus* wood (17%) (Ngernyen et al., 2006), *Eucalyptus camaldulensis* Dehn wood (33%) (Jindaphunphairoth, 2000), *Eucalyptus globules* wood (23%) (Arriagada et al., 1994) and *Eucalyptus grandis* sawdust (31%) (Tancredi et al., 1996). This was because in chemical activation processes, washing is required in order to remove any residual of dehydrating agents and this consequently resulted in the loss of a large amount of carbon mass. This washing step is not necessary for the physical activation process and therefore a high carbon yield could be achieved. On the other hand, the

activated carbon from physical processes provide relatively lower levels of iodine number and BET surface area (in this work, these were  $693 \text{ mg g}^{-1}$ ,  $794 \text{ m}^2 \text{ g}^{-1}$ , respectively) when compared to those from other activation methods such as chemical activation by phosphoric acid of Thongton (2008) and Patnukao et al. (2008) ( $917 \text{ mg g}^{-1}$ ,  $1239 \text{ m}^2 \text{ g}^{-1}$  and  $1226 \text{ mg g}^{-1}$ ,  $1457 \text{ m}^2 \text{ g}^{-1}$ , respectively). This could well be due to the fact that the washing removes the residual tar and ash from the carbon structure leaving a more complex and interconnected network porous structure, and a higher BET surface area becomes more apparent. In addition, activated carbon from the physical activation of *Eucalyptus camaldulensis* Dehn bark possessed lower levels of iodine number and BET surface area when compared to other raw materials such as *Eucalyptus camaldulensis* Dehn wood ( $1233 \text{ mg g}^{-1}$ ,  $1076 \text{ m}^2 \text{ g}^{-1}$ ) (Jindaphunphairoth, 2000), *Eucalyptus globules* wood ( $968 \text{ mg g}^{-1}$ ,  $1193 \text{ m}^2 \text{ g}^{-1}$ ) (Arriagada et al., 1994) and *Eucalyptus grandis* sawdust ( $1193 \text{ m}^2 \text{ g}^{-1}$ ) (Tancredi et al., 1996). This could be because eucalyptus bark contains lower carbon content and cellulose than eucalyptus wood and sawdust, i.e. the carbon content and cellulose content from eucalyptus bark were 42.6% (this work) and 32% (Yadav et al., 2002), respectively, whilst eucalyptus wood contains carbon and cellulose at 57.2% and 65% (Kumar et al., 1992), respectively (see Table 4.5). Raw materials with a higher content of cellulose were often reported to yield activated carbon with a predominantly microporous structure (Ioannidou et al., 2007), because cellulosic content could be activated at a higher rate than lignin (Daud and Ali, 2004). Lastly, the property of raw materials (eucalyptus) from this work is compared with the others reports as illustrated in Table 4.6, e.g. BET surface area of activated carbons from various sources are: Coconut shell ( $525 \text{ m}^2 \text{ g}^{-1}$ ) (Achaw et al., 2008), Corncob ( $675 \text{ m}^2 \text{ g}^{-1}$ ) (Aworn et al., 2008), Rubberwood sawdust ( $1096 \text{ m}^2 \text{ g}^{-1}$ ) (Kumar et al., 2006), Birch ( $450 \text{ m}^2 \text{ g}^{-1}$ ) (Zanzi et al., 2001) and Plam oil ( $284 \text{ m}^2 \text{ g}^{-1}$ ) (Suwansangchoto, 1999).

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Table 4.4 Comparison of Eucalyptus-derived activated carbons

Reference	Raw material	Carbonization	Activation	Activating agent	Yield (%)	Iodine number (mg g <sup>-1</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
This work	Eucalyptus <i>camaldulensis</i> Dehn bark	500°C for 45 min	900°C for 2 h.	Steam	52.5	693	794
Thongton (2008)	Eucalyptus <i>camaldulensis</i> Dehn bark	-	500°C for 1 h.	H <sub>3</sub> PO <sub>4</sub>	30.5	917	1239
Patnukao et al. (2008)	Eucalyptus <i>camaldulensis</i> Dehn bark	-	500°C for 1 h.	H <sub>3</sub> PO <sub>4</sub>	26.0	1226	1457
Ngernyen et al. (2006)	Eucalyptus wood	400°C for 40 min. with N <sub>2</sub> and a heating rate of 25°C min <sup>-1</sup>	900°C for 1 h.	CO <sub>2</sub>	17.0	-	1496

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Table 4.4 Comparison of Eucalyptus-derived activated carbons (continued)

Reference	Raw material	Carbonization	Activation	Activating agent	Yield (%)	Iodine number (mg g <sup>-1</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
Jindaphunphairoth (2000)	Eucalyptus <i>camaldulensis</i> Dehn wood	450°C for 45 min	900°C for 2.5 h.	Steam	33	1233	1076
Tancredi et al. (1996)	Eucalyptus <i>grandis</i> sawdust	800°C for 2 h. with N <sub>2</sub> and a heating rate of 10°C min <sup>-1</sup>	800°C for 1 h.	Steam	23	-	1190
Arriagada et al. (1994)	Eucalyptus <i>globules</i> wood	450°C for 2 h.	900°C for 4.5 h.	Steam	23	968	1193

Table 4.5 Properties of eucalyptus raw materials

Reference	Raw material	Carbon content (%)	Cellulose (%)	Lignin (%)
This work	Eucalyptus bark	42.6	-	-
Amaya et al. (2007)	Eucalyptus wood	47.1	-	-
Guerrero et al. (2005)	Eucalyptus wood	48.7	-	-
Yadav et al. (2002)	Eucalyptus bark	-	37	28
Kumar et al. (1992)	Eucalyptus wood	57.2	65	35

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Table 4.6 Comparison of steam-derived activated carbons obtained from this work and other reports

Reference	Raw material	Carbonization	Activation	Yield (%)	Iodine number (mg g <sup>-1</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )
This work	Eucalyptus camaldulensis <i>Dehn</i> bark	500°C for 45 min	900°C for 2 h.	52	693	794
Achaw et al. (2008)	Coconut shell	325°C for 150 min	800°C for 2 h.	-	-	525
Aworn et al. (2008)	Corncob	500°C for 60 min	800°C for 2 h.	-	-	675
Li et al. (2008)	Coconut shell	1000°C for 2 h.	900°C for 2 h.	-	-	1926
Prakash et al. (2006)	Rubberwood sawdust	400°C for 60 min	750°C for 1 h.	-	765	1092
Zanzi et al. (2001)	Birch	-	650°C for 2 h.	25-12	-	450
Suwansangchoto (1999)	Plam oil	300°C for 30 min	850°C for 6 h.	7	404	284

#### **4.4 Optimal activation condition by CO<sub>2</sub>**

Physical activation using carbon dioxide or steam as oxidizing agents are the most commonly used processes in the production of activated carbon. This experiment focuses the optimal activation condition by steam (900°C) in order to compare the results with those from the carbon dioxide activation. The property of activated carbon obtained from the experiment is shown in Table 4.7.

##### **4.4.1 Yield**

Table 4.7 demonstrates that %yield of activated carbon decreased while activation temperature increased owing to the gasification of surface carbon atoms. In other words, high temperature caused a more rigorous and rapid removal of gaseous products, volatile matters and tars out of the carbon structure, and so lowering the carbon yield of the activated carbon. Note that the remaining volatile matter that stayed deeper in the carbon structure needed a longer time to diffuse out of the char structure.

##### **4.4.2 Bulk density**

Table 4.7 illustrates that an increase in the activation time resulted in a decrease in the bulk density of the activated carbon product. Carbon dioxide as the activating agent reacted with charcoal and volatile matter and diffused quickly out of the surface of carbon structure during the activation process. Therefore, with high temperature, the gasification of surface carbon atoms became the predominant reaction which led to low bulk density.

##### **4.4.3 Ash content**

Table 4.7 demonstrates that % ash content in activated carbon increased with activation time period. This could be that carbon dioxide as the activating agent oxidized with carbon element in charcoal. With an increase of the activation temperature, the rate of the chemical reaction also increased, and at adequately high temperature, the oxidation rate became so high that significant losses of the carbon material occurred. Ash is normally not removed from this reaction, and therefore the fraction of ash became higher when other carbon components were being gasified.

Table 4.7 Characteristics of activated carbon from Eucalyptus bark by carbon dioxide activation

Activation		Yield (%)	Ash (wt %)	Bulk density (g cm <sup>-3</sup> )	Iodine number (mg g <sup>-1</sup> )
Temperature (°C)	Time (min)				
850	120	68.5	24.8	0.47	209±41
900	60	67.2	25.3	0.46	316±26
	90	64.0	28.9	0.40	322±11
	120	58.5	30.9	0.39	352±15
950	120	52.7	32.0	0.41	483±17

#### 4.4.4 Iodine number

Table 4.7 indicates that iodine number increased with an increase in activation temperature. This was because, at high temperature, the reaction of carbon dioxide as the activating agent with carbon structure did not only result in the development of micropore and the opening of blocked pores by devolatilization process leading to the formation of new micropores, but did also cause the widening of existing micropore by gasification reaction and possibly by the collapse of neighboring pore walls. Therefore, with high temperature, the activating agent could be easily diffuse to the carbon structure, resulting in the carbon product with high iodine number.

Similar to the activation temperature, the activation time was also an important factor controlling the property of the activated carbon such as the iodine number. Iodine number increased from 316 to 352 mg g<sup>-1</sup> with an increasing holding time from 60 to 120 minutes. This was a consequence of increasing rate of reaction between carbon and carbon dioxide which led to the enhancement of the devolatilization and thermal degradation. This then resulted in the opening of pores and even the loss of some walls among the pores.

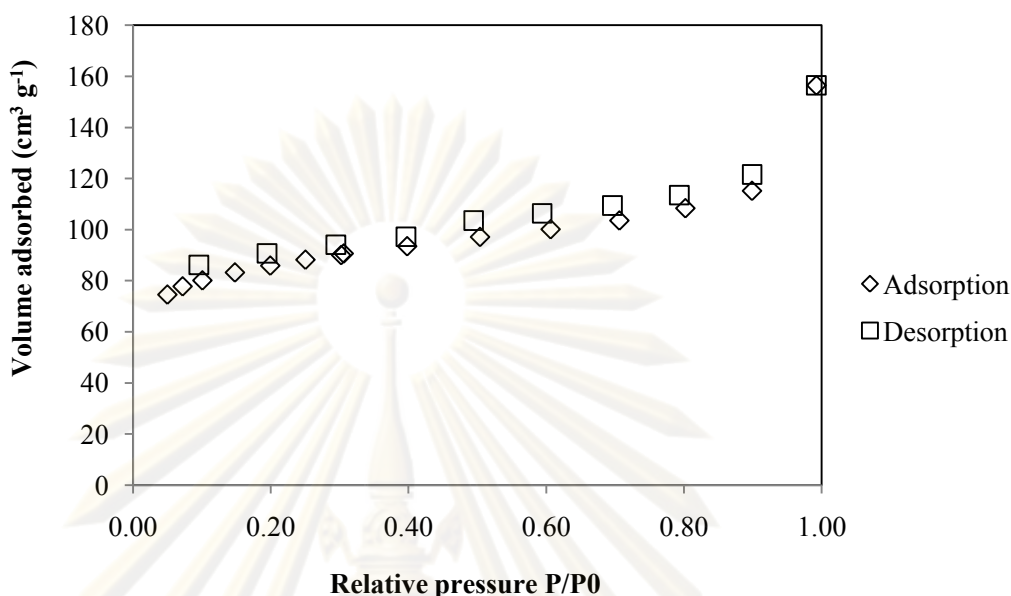


Figure 4.11 N<sub>2</sub> adsorption and desorption isotherms at 77K on CO<sub>2</sub> activated carbon

#### 4.4.5 Surface area and pore volume

Table 4.7 shows the results obtained from the carbon dioxide activation where the highest value of the iodine number (483 mg g<sup>-1</sup>) was obtained from the activation at 950°C for 120 minutes. This work, nevertheless, focused mainly on carbon dioxide activation at 900°C for 120 minutes to enable the comparison with the steam activation at the same condition.

Adsorption characterization for activated carbon was determined via nitrogen adsorption at 77K and a relative pressure ( $P/P_0$ ) range of 0.0-1.0. The Brunauer–Emmett–Teller (BET) total surface area was assumed such that the sorption at surface was monolayer. The pore size distribution was estimated using the Barrett–Joiner–Halenda (BJH) equation during the desorption phase. Figure 4.11 illustrates N<sub>2</sub> adsorption-desorption isotherms at 77K on the carbon dioxide activated carbon where the shape of isotherm could be identified as Type I. Table 4.8 provides the BET surface area and pore volume of carbon dioxide activated carbon which indicates that the activated carbon from carbon dioxide activation exhibited a relatively low BET surface (274 m<sup>2</sup> g<sup>-1</sup>) when compared with other carbon dioxide activated carbons such as Almond tree pruning (1080 m<sup>2</sup> g<sup>-1</sup>) (Gonzalez et al., 2009), Corncob (820 m<sup>2</sup> g<sup>-1</sup>) (Aworn et al., 2009) and Walnut shell (792 m<sup>2</sup> g<sup>-1</sup>) (Gonzalez et al., 2009). The total

pore volume of  $0.242 \text{ cm}^3 \text{ g}^{-1}$  consisted of micropore and mesopore in the proportion of 69% and 31%, respectively.

Table 4.8 Properties of activated carbon from carbon dioxide activation

Properties	Value
<i>Ultimate analysis (wt %)</i>	
C	61.68
H	0.58
N	0.31
O,S (balance)	37.43
<i>Physical properties</i>	
Yield (wt %)	58.5
Ash (wt %)	30.9
Bulk density ( $\text{g cm}^{-3}$ )	0.39
Iodine number ( $\text{mg g}^{-1}$ )	$352 \pm 15$
BET Surface area ( $\text{m}^2 \text{ g}^{-1}$ )	274
- Micropore (%)	69
- Mesopore (%)	31
- Average pore diameter ( $\text{\AA}$ )	35.39
- Total pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )	0.242

The property of the carbon dioxide activated carbon at  $900^\circ\text{C}$  120 minutes is illustrated in Table 4.8. The carbon dioxide activated carbon exhibited carbon content of 61.68%, ash content 37.3%, yield 58.5%, bulk density  $0.37 \text{ g cm}^{-3}$ , iodine number  $352 \text{ mg g}^{-1}$  and surface area  $274 \text{ m}^2 \text{ g}^{-1}$ . As a general observation, at the same activation conditions, the iodine number of activated carbon activated by carbon dioxide was found to be relatively lower than that activated by steam (see Tables 4.3 and 4.8). However, the two activating agents produced similar microporosity, steam produced a slightly narrower microporosity than carbon dioxide. This may be because the molecule of water smaller than carbon dioxide, and consequently steam diffused more rapidly into the porous network and more easily accessed the carbon structure. Accordingly, carbon dioxide activation needs a slightly higher temperature and time

activation to increase the gasification rate in order to increase the surface area when compared with steam activation.

#### **4.5 Characterization of activated carbon**

##### **4.5.1 FTIR**

Chemical characterization was carried out by FTIR spectroscopy in order to identify functional groups at the surface of carbon materials. The FTIR spectra of charcoal, steam and carbon dioxide activated carbon are shown in Figures 4.12-4.14 and the assignments of IR absorption bands are collected in Table 4.10.

The assignment of absorption bands shows that functional groups like alkene, aromatic, ketone, alcohol, hydroxyl and carboxyl were present in the carbonized products. These functional groups could be derived from the eucalyptus bark raw material, which are essentially composed of cellulose, hemicellulose and lignin. After activation by steam, the band at  $3642.83\text{ cm}^{-1}$  appeared which indicated that the reaction between steam and carbon atom in charcoal led to a formation of non-bonded OH groups. The IR absorption bands of steam activation carbon exhibited a lower intensity than carbonization product. This change in intensity was a consequence of the activating reaction of steam where oxygen and hydrogen groups were decomposed and extracted from the surface. The IR spectra obtained for carbon dioxide activated carbon exhibited a similar shape, which shows that the same functional groups were present in the carbon dioxide activated carbon product.

Table 4.9 Summarises the functional groups presented in the charcoal and final activated carbon product.

Samples	Functional groups
Charcoal	<ul style="list-style-type: none"> <li>- alkene,</li> <li>- aromatic,</li> <li>- ketone,</li> <li>- alcohol,</li> <li>- hydroxyl</li> <li>- carboxyl</li> </ul>
Steam activated carbon	<ul style="list-style-type: none"> <li>- oxygen and hydrogen groups</li> <li>- aromatic groups</li> </ul>
Carbon dioxide activated carbon	<ul style="list-style-type: none"> <li>- oxygen and hydrogen groups</li> <li>- aromatic groups</li> </ul>

Table 4.10 FT-IR spectra results from the activated carbon product

Assignment	Frequency (cm <sup>-1</sup> )
Non-bonded OH groups	>3500
O-H stretching	3400-3500
Stretching in aldehydes, ketones groups and esters	1800-1450
Aromatic and oxygen functional groups	1750-900
Skeletal C=C vibrations in the aromatic rings	1660-1430
Stretching in aromatic skeletal and ester	1444
O-H bending-in plane	1440-1410
Phenols and alcohol groups	1400-1300
alkenes	874

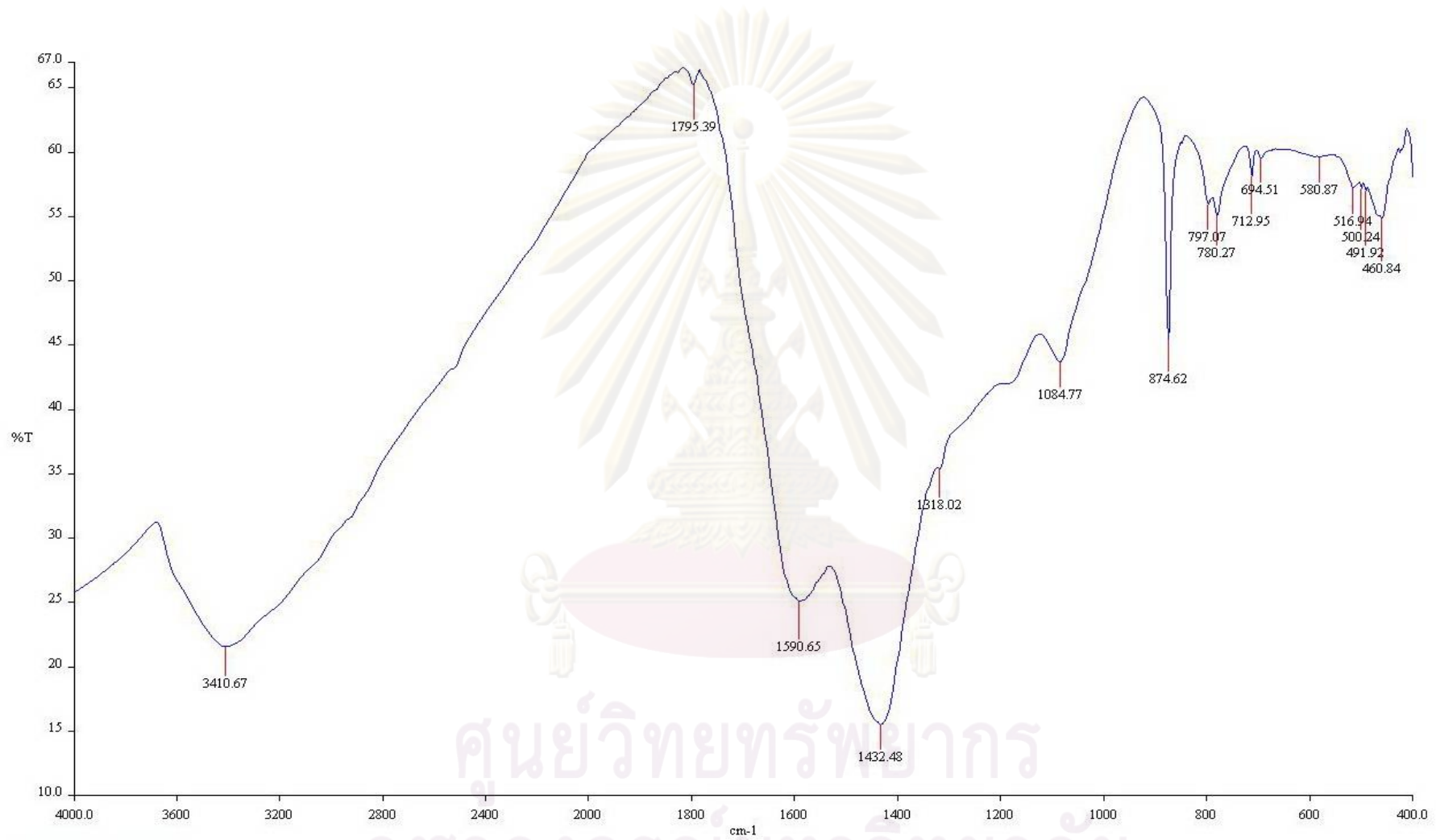


Figure 4.12 FT-IR transmission spectra of charcoal



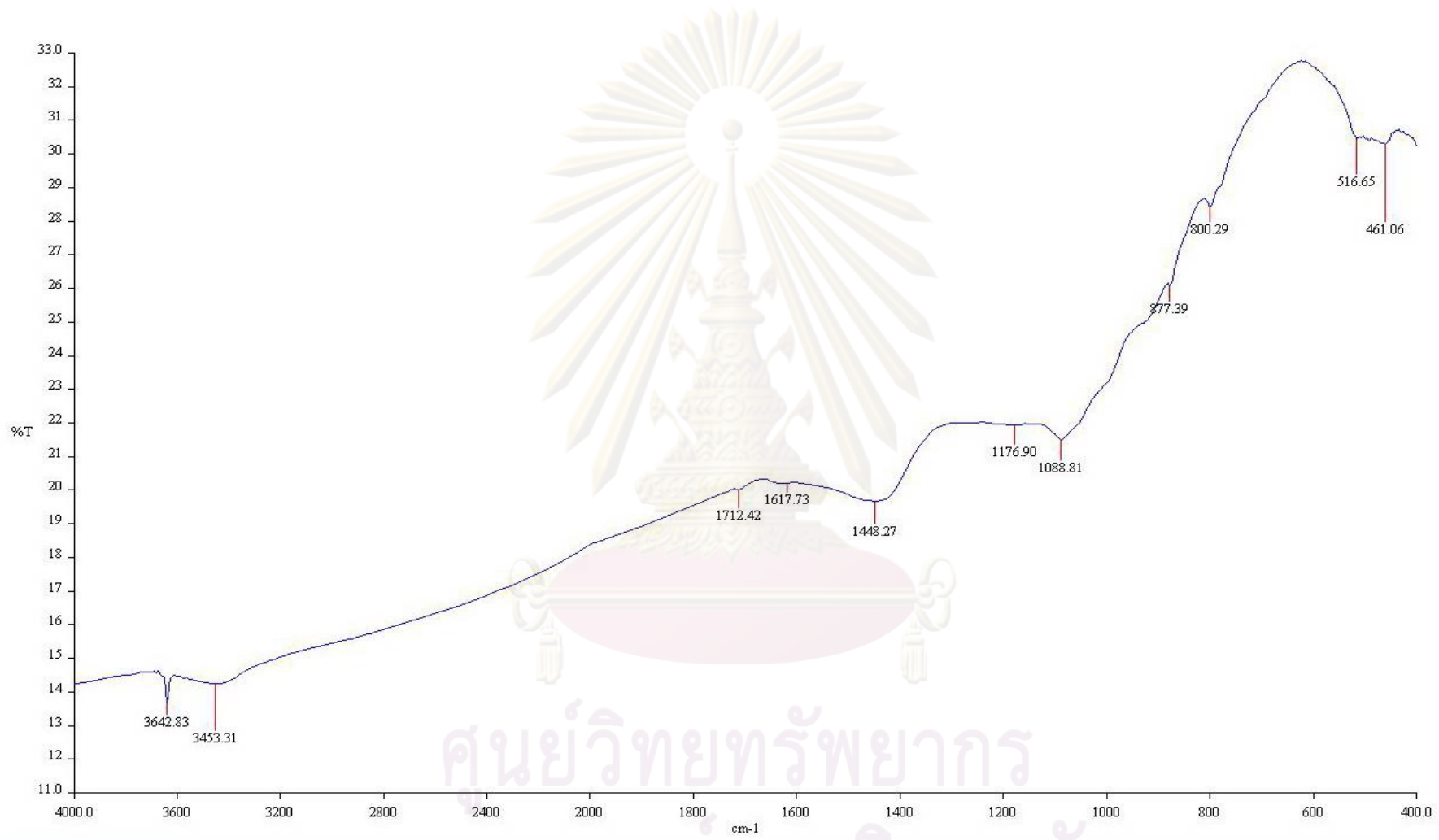


Figure 4.13 FT-IR transmission spectra of steam activated carbon

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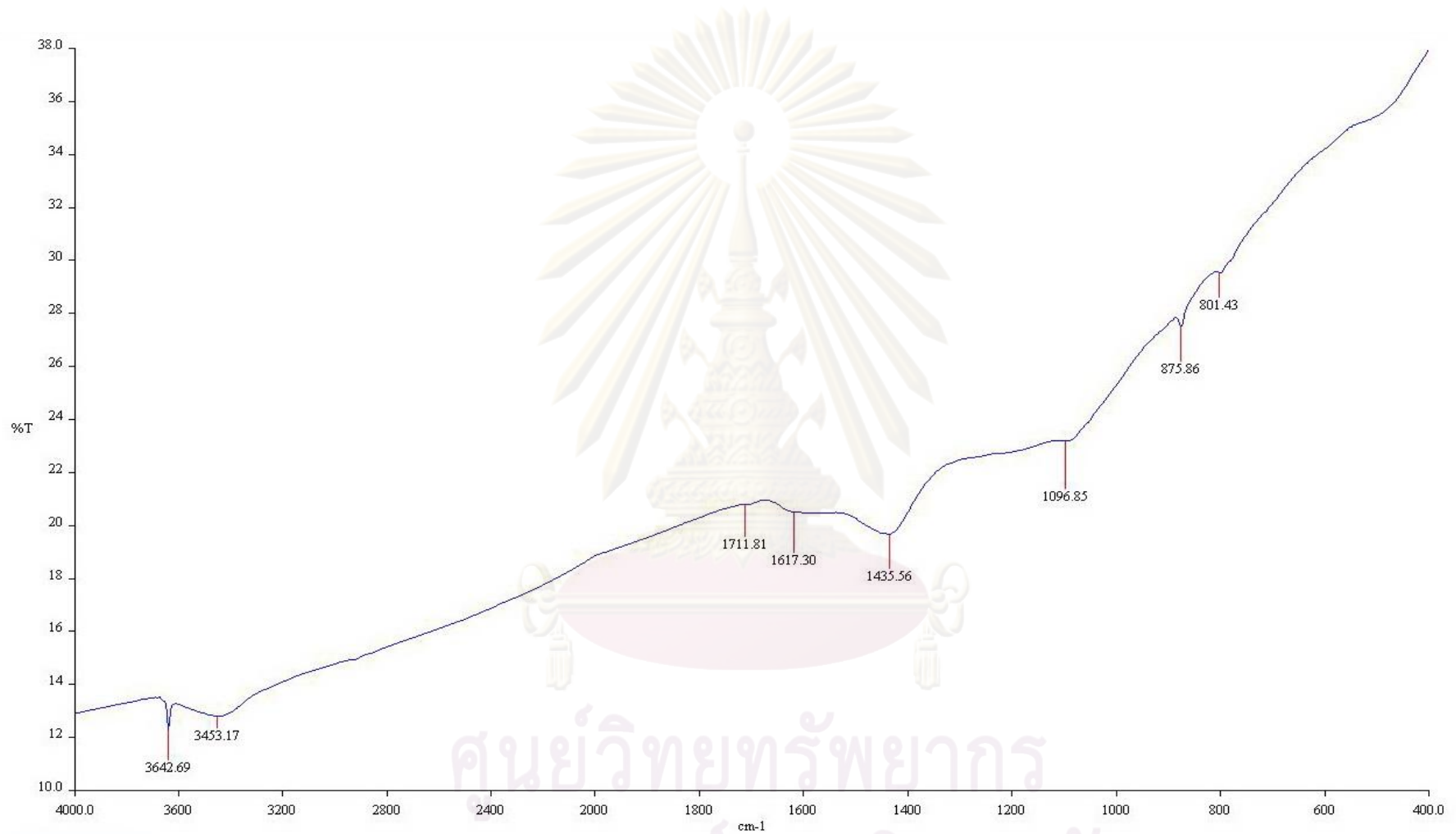


Figure 4.14 FT-IR transmission spectra of carbon dioxide activated carbon

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#### 4.5.2 XRD

X-ray diffraction (XRD) patterns of steam and carbon dioxide activated carbons are given in Figures 4.15 and 4.16. The XRD pattern of steam activated carbon at 900°C for 120 minutes (optimal synthetic condition) exhibited amorphous carbon structure. Generally, the activation process could be divided into two stages: firstly the gasification of the carbon atoms out of the crystalline structure, introducing micropores among crystallites, and secondly, the gasification of these crystallites to form pore networks including mesopores and macropores (Lazaro et al., 2007). On the other hand, the XRD pattern of carbon dioxide activated carbon at the same synthetic condition with that of steam activation revealed that this condition might not be optimal because there were a few diffraction peaks emerged from the base line which represented the presence of a small amount of crystalline matter. This could be due to the existence of residual volatile matter or tar in the deeper pore in carbon structure. This resulted in the lower BET surface area and iodine number

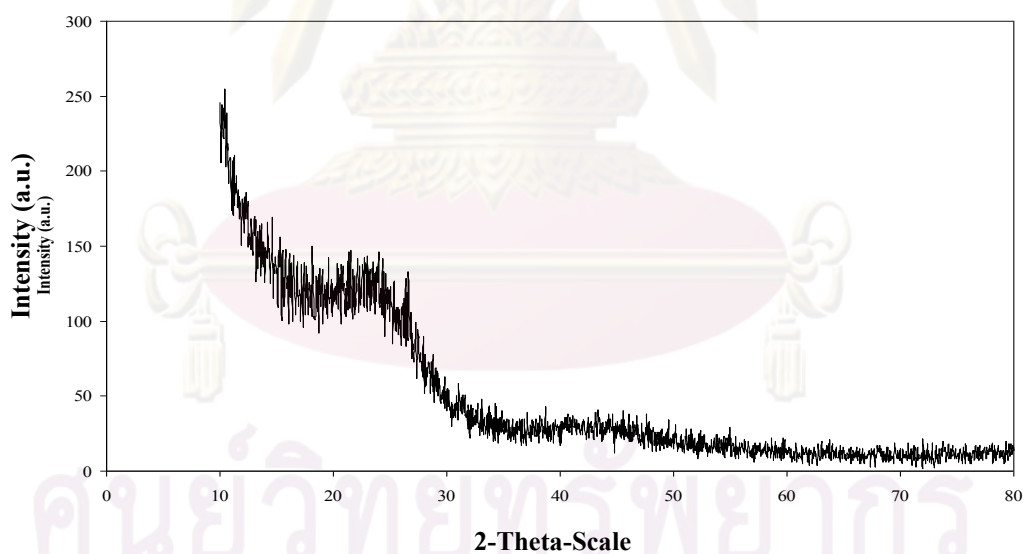


Figure 4.15 XRD patterns of steam activated carbon

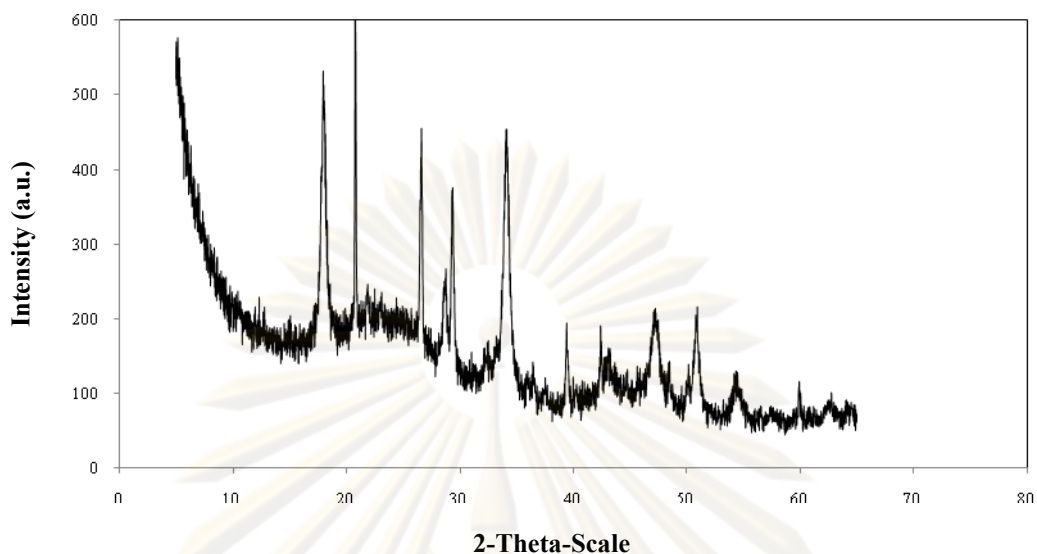
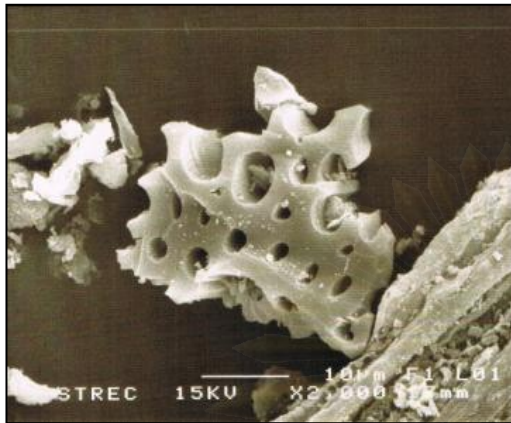


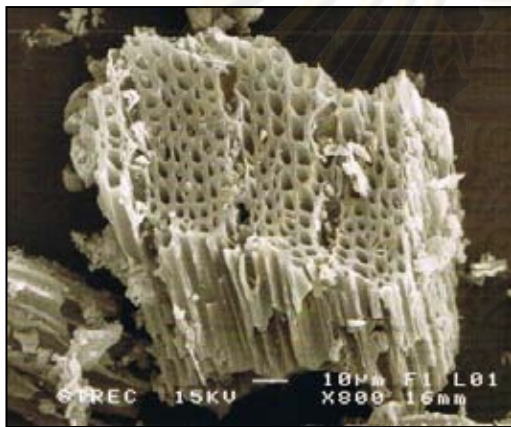
Figure 4.16 XRD patterns of carbon dioxide activated carbon

#### 4.5.3 SEM

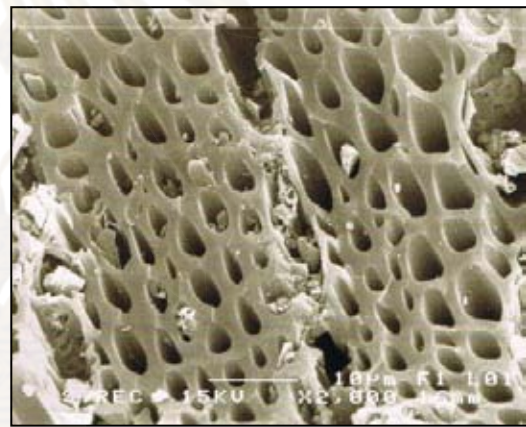
The effect of different activation processes on the eucalyptus bark precursors is clearly observed from the Scanning electron microscopy (SEM) in Figure 4.17, i.e. carbonization at 500°C 45 minutes in Figure 4.17(a), steam activation at 900°C 120 minutes in Figure 4.17(b),(c), and carbon dioxide activation at 900°C 120 minutes in Figure 4.17 (d),(e). The carbonization process resulted in a lower pore volume, high volatile matter and tar content carbon product. This was because this step only involved low temperature, which was not able to completely burn away the impurity during the carbonization process, and therefore these impurities remained in the pores after carbonization (see Figure 4.17 (a)). After activation by an activating agent (steam and carbon dioxide), the porosity is better developed due to the elimination of volatile matters. The activated carbon activated by carbon dioxide and steam had the surface with macropores with a diameter of around 1.5-8.5  $\mu\text{m}$  and 4.5-9  $\mu\text{m}$ , respectively (Figure 4.17 (b)-(e)). This is beneficial for most adsorption processes because large sized pores serve as feeder pores to lower dimension ones, i.e., meso- and micropores (Table 4.3 and 4.8). From the comparison of steam activated carbon (Figure 4.17 (b), (c)) and carbon dioxide activated carbon (Figure 4.17 (d), (e)), it can be inferred that steam activation led to a narrower pore size distribution and pore volume than carbon dioxide activation (Tables 4.3 and 4.8).



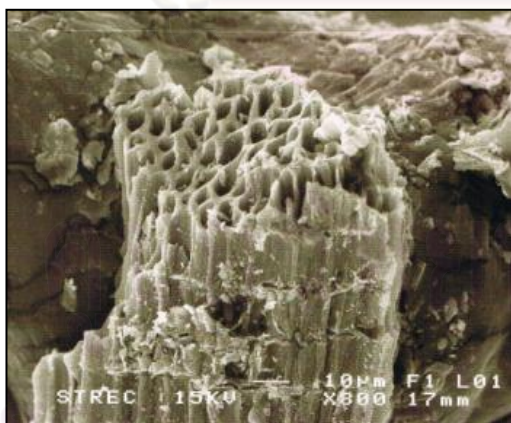
(a)



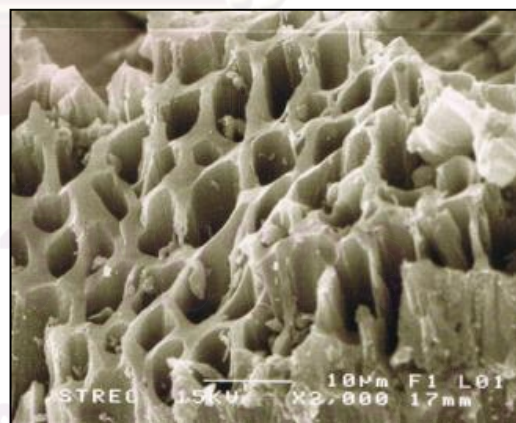
(b)



(c)



(d)



(e)

Figure 4.17 SEM micrographs of Eucalyptus bark activated carbon: (a) charcoal 2000X, (b) steam-activated carbon 800X, (c) steam-activated carbon 2000X, (d) CO<sub>2</sub>-activated carbon 800X, (e) CO<sub>2</sub>-activated carbon 2000X

## 4.6 Adsorption study

### 4.6.1 Effect of pH for adsorption

The pH of solution has been identified as the most important variable governing metal adsorption on the adsorbent (Wang et al., 2009). This is because hydrogen ion is competing with the positively charged metal ions on the active sites of the adsorbent. The effect of pH on adsorption of Pb (II) ion on steam activated carbon has been examined by allowing the adsorption in the controlled environment with different pH levels (range from 1–5) and the results are shown in Figure 4.18. This pH range was chosen in order to avoid metal solid hydroxide precipitation. The results indicate that the maximum adsorption of Pb(II) was obtained at pH 4 ( $q_e = 3.9$  mg g<sup>-1</sup>) The equilibrium adsorption amount of Pb (II) on steam activated carbon increased with increasing pH as a result of a decrease in competition between protons (H<sup>+</sup>) and positively charged metal ions at the surface sites (Boudrahem et al., 2009). The sorption decreased at higher pH (pH >5.0) which was possibly due to the metal hydrolysis and potential precipitation. Subsequent studies are thereafter conducted at pH 4.



Figure 4.18 Effect of pH on adsorption (Amount of activated carbon = 0.1 g, initial lead concentration = 10 mg L<sup>-1</sup>, shaking rate = 200 rpm, temperature = 30°C)

#### 4.6.2 Adsorption isotherm

The adsorption isotherms reveal the specific relation between adsorption capacity and concentration of the remaining adsorbate at constant temperature. Several models have been used in the literature to describe experimental adsorption data. Freundlich and Langmuir models are the two most frequent used. In this work both models were used to quantify the adsorption capacity of steam activated carbon for the removal of Pb(II) ions from synthetic wastewater.

Langmuir isotherm is based on the monolayer sorption of lead ions on the surface of carbon sites and is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \left(\frac{1}{q_m}\right)C_e \quad (4.3)$$

where  $C_e$  and  $q_e$  are the remaining concentration of Pb(II) ions after equilibrium ( $\text{mg L}^{-1}$ ) and the amount of adsorbed lead at equilibrium, respectively,  $q_m$  and  $b$  the total number of surface sites per mass of sorbent ( $\text{mg g}^{-1}$ ) and Langmuir constant or capacity factor. Figure 4.20 illustrates the plots of Pb(II) ions which shows that a straight line could be well observed between  $1/q_e$  and  $1/C_e$ . This implies that the isotherm data fitted the Langmuir equation quite well ( $R^2 = 0.9964$ ). The values of  $q_m$  and  $b$  determined from the Langmuir plot were  $54.6 \text{ mg g}^{-1}$  and  $0.02 \text{ L mg}^{-1}$ , respectively.

Freundlich isotherm describes the heterogeneous surface energies by multilayer sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (4.4)$$

where  $K_F$  and  $n$  are constants of Freundlich isotherm incorporating adsorption capacity ( $\text{mg g}^{-1}$ ) and intensity. The isotherm data fitted the Freundlich model relatively well with an  $R^2$  of 0.9215. The values of the constants  $K_F$  and  $1/n$  were calculated to be 2.1 and 0.40, respectively. The value of  $1/n$  of less than 1 indicates a favorable adsorption. The Langmuir and Freundlich isotherm parameters are summarized in Table 4.11. The Langmuir and Freundlich isotherm parameters obtained from this work fall in the same range as those reported in literature (for other natural materials) (Table 4.12).

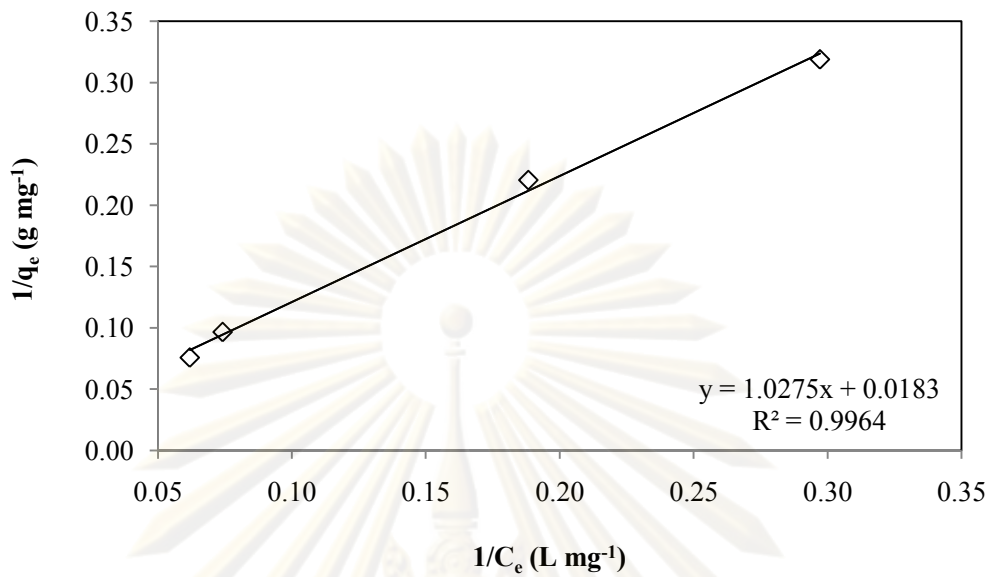


Figure 4.19 Langmuir isotherm plots for adsorption of Pb(II) on to activated carbon (amount of activated carbon = 0.1 g, time 30 minutes, shaking rate = 200 rpm, temperature = 30°C, pH = 4)

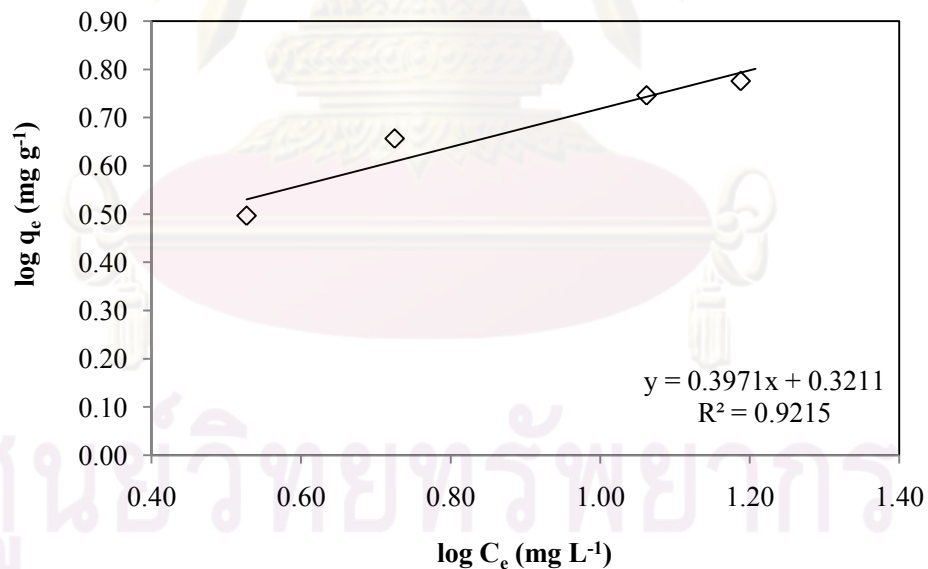


Figure 4.20 Freundlich isotherm plots for the adsorption of Pb(II) on to activated carbon (amount of activated carbon = 0.1 g, time 30 minutes, shaking rate = 200 rpm, temperature = 30°C, pH = 4)



Table 4.11 Langmuir and Freundlich isotherm parameters

Langmuir isotherm			Freundlich isotherm		
$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$	$1/n$	$R^2$
54.6	0.02	0.9964	2.1	0.4	0.9215

Table 4.12 Comparison of lead adsorption by activated carbon

Reference	Raw material	Langmuir isotherm		Freundlich isotherm	
		$q_m$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$K_F$	$1/n$
This work	Eucalyptus bark	54.6	0.02	2.1	0.4
Boudrahem et al. (2009)	Coffee residue	63.3	0.40	27.5	0.2
Patnukao et al. (2008)	Eucalyptus bark	184.4	0.01	0.46	0.5
Rafatullah et al. (2009)	meranti sawdust	34.2	0.02	1.5	1.0
Acharya et al. (2009)	Tamarind wood	43.9	0.27	9.3	0.7

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# CHAPTER V

## CONCLUSIONS AND RECOMMENDATION

### 5.1 Conclusions

The Eucalyptus bark has great potential as a precursor in the production of activated carbon as it contains high carbon content and low ash. The optimal carbonization condition for the production of charcoal from eucalyptus bark was 500°C for 45 minutes. This condition yielded a suitable amount of volatile matter of 24.2%. The best condition of steam activation was at 900°C for 120 minutes. This condition gave the highest iodine number and BET surface area (693 mg g<sup>-1</sup> and 794 m<sup>2</sup> g<sup>-1</sup>, respectively).

Steam activation and carbon dioxide activation gave activated carbon with different characters at same condition as summarized below:

Steam activation	Carbon dioxide activation
- High iodine number (693 mg g <sup>-1</sup> )	- Low iodine number (352 mg g <sup>-1</sup> )
- High BET surface areas (794m <sup>2</sup> g <sup>-1</sup> )	- Low BET surface area (274 m <sup>2</sup> g <sup>-1</sup> )
- High pore volumes (0.555 cm <sup>3</sup> g <sup>-1</sup> )	- Low pore volumes (0.242 cm <sup>3</sup> g <sup>-1</sup> )
- Mainly micropores (84%)	- Mainly micropores (69%)

The sorption of lead onto steam-activated carbon depended on solution pH, contact time and initial concentration of Pb (II). The maximum sorption uptake was achieved at pH 4 for 30 minutes. Moreover, the adsorption studies showed the adsorption characteristics as summarized below:

- The adsorption of Pb (II) was rapid with complete adsorption within 30 minutes.
- Experimental data fitted better with Langmuir than Freundlich isotherm
- Langmuir isotherm parameters were  $q_m$  54.6 mg g<sup>-1</sup>,  $b$  0.02 L mg<sup>-1</sup>
- Freundlich isotherm parameters were  $K_F$  2.1,  $1/n$  0.4

## 5.2 Contributions

This research utilized eucalyptus bark waste from pulp and paper industry as a source material for the production of activated carbon by steam and carbon dioxide activation. It was illustrated that physical conversion of the bark was possible and the final product exhibited a reasonably well sorption property. When compared to chemical activation methods, due to the absence of chemical requirements, the physical activation method requires no washing step which not only prevents the generation of wastewater, but also reduces the chemical demands which makes it more attractive in environmental point of view. However, physical treatment requires that the carbon be extensively thermal treated which needs more energy inputs than the chemical activation. Based on our preliminary calculation, the energy inputs for the physical method were about 6 times more than the chemical method, i.e. the energy requirement for the production of 100g activated carbon is 19 units for the physical treatment and 3.1 units for the chemical method. However, this did not include the cost of chemicals, water, water treatment, and wastewater treatment that will occur during the chemical method (the exact cost still cannot be evaluated from this work).

The results from this work could be used further to mitigate the disposal problem of excess Eucalyptus bark by converting this waste material to a valuable product such as activated carbon.

## 5.3 Recommendations

Based on the results of this study, some recommendations for future studies can be proposed.

1. This work used horizontal tubular furnace which could encounter a distribution problem of gas flow through the furnace. This uneven flow distribution could then lead to a lower reaction rate between carbon atom and activating agent, resulting in a less developed porosity and lower surface area. Future work should look at the performance of the vertical tubular furnace which could alleviate this problem.

2. Engineering aspect of this system should also be considered especially in terms of energy efficiency. The use of waste heat in the factory in heating the furnace is highly crucial for the economical feasibility of this work

3. The activated carbon might be applied for the adsorption of several metal ions. This work demonstrated the adsorption of lead which is the positively charged ion, and therefore the adsorption of other metal ions such as lead, copper, cadmium, phenol, arsenic, mercury and chromium, could also be possible. This should be investigated further.



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**APPENDICES**

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## APPENDIX A.1

### Determination for Ash Content (ASTM D 2866-94)

#### Apparatus

- *Muffle Furnace*, having air circulation, capable of temperature regulation of  $\pm 25^{\circ}\text{C}$  at  $650^{\circ}\text{C}$
- *High-Temperature Crucible*, high-form
- *Analytical Balance*, having a sensitivity of 0.1 mg
- *Desiccator*
- *Oven*, forced-air circulation, capable of temperature regulation between  $145$  and  $155^{\circ}\text{C}$

#### Procedure

1. Ignite the crucible in the muffle furnace at  $650 \pm 25^{\circ}\text{C}$  for 1 h. Place the crucible in the desiccator. Cool to room temperature and weigh to the nearest 0.1 mg.
2. Dry an adequate sample of activated carbon to constant weigh at  $150 \pm 5^{\circ}\text{C}$  (3 h 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  $650 \pm 25^{\circ}\text{C}$ . Ashing will require from 3 to 16 h, 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. Weight to the nearest 0.1 mg.

#### Calculation

- Calculate the ash content as follows:

$$\text{Total ash, \%} = \frac{(D - B)}{(C - B)} \times 100 \quad (\text{A.1-1})$$

- where :
- $B$  = weight of crucible, g
  - $C$  = weight of crucible plus original sample, g
  - $D$  = weight of crucible plus ashed sample, g

## APPENDIX A.2

### Determination for Apparent Density (ASTM D 2854-89)

#### Apparatus

- *Reservoir Funnel*, fabricated of glass or metal
- *Feed Funnel*, also of glass or metal
- *Metal Vibrator*, 26-gage galvanized sheet metal
- *Cylinder*, graduated, 100 mL capacity
- *Balance*, having a sensitivity of 0.1 g

#### Procedure

1. Dry an adequate sample of the carbon to be tested to constant weight at  $150 \pm 5^\circ\text{C}$ .
2. Carefully place a representative sample of the activated carbon into the reservoir funnel so that the material does not prematurely flow into the graduated cylinder. If this occurs, return the material to the reservoir funnel.
3. Add the sample to the cylinder using to vibrator feeder through the feed funnel having a stem 23.8 mm (15/16 in.) in inside diameter.
4. Fill the cylinder at a uniform rate not less than 0.75 or exceeding 1.0 mL/s, up to the 100 mL mark. The rate can be adjusted by changing the slope of the metal vibrator or raising or lowering the reservoir funnel, or both.
5. Transfer the contents from the cylinder to a balance pan and weigh to the nearest 0.1 g.

#### Calculation

- For predried samples, calculate the apparent density as follows:

$$\text{Apparent density, g/mL} = \frac{\text{weight of activated carbon}}{100} \quad (\text{A.2-1})$$

- For samples that have not been predried, calculated the apparent density on the dry basis as follows:

$$\text{Apparent density, g/mL} = 10^{-4} (\text{weight of activated carbon, g}) \times (100 - \% \text{ moisture}) \quad (\text{A.2-2})$$

### APPENDIX A.3

#### Determination for Chemical Analysis (ASTM D 1762-84)

##### Apparatus

- *Mill*, for grinding samples
- *Oven*, with automatic temperature control at  $105 \pm 1$  °C
- *Muffle Furnace*, to control temperature at  $750 \pm 5$  °C and  $950 \pm 5$  °C
- *Analytical balance*, with a capacity of at least 100 g and a sensitivity of 0.1 mg
- *Containers*, airtight, such as screw-top bottles for storage of ground samples
- *Sieves*, as specified in Method D 410
- *Crucibles*, porcelain, 41 by 37 mm with porcelain lids
- *Desiccator*, containing calcium chloride as drying agent

##### Sample

1. *Sample Selection*-The sample shall be selected so as to be representative of all of the material contained in a lot. Sample selection shall be carried out in accordance with Practices D 346, D 3176, and D 3180.
2. *Sample Preparation*-Samples will normally be air-dry charcoal lumps or briquets. Rainsoaked or wet samples shall be spread out to air-dry before carrying out the analysis. For purchase specification, the moisture content of the charcoal, as received, shall be determined on samples ground to pass No.20 (850- $\mu$  m) sieve ,since excessive grinding will result in loss of moisture due to the generation of heat . For laboratory evaluation, moisture, ash, and volatile matter shall be determined on a sample ground as follows:
  - 2.1 All of the selected sample shall be ground; no part of the sample shall be rejected. The sample shall be pulverized rapidly in a mill. Long grinding time shall be avoided because of generated heat which will cause loss of volatile material. Excessive grinding will produce a large amount of fine particles smaller than a No. 100 (150- $\mu$  m)



sieve. These fine particles contribute to errors of being swept out of the crucible during the rapid evolution of gases in the determination of volatile matter. Particles that will be retained on a No. 20 (850- $\mu$  m) sieve shall not be used. The ground sample shall be well mixed and stored in an airtight container.

### Procedure

1. Make duplicate determinations.
2. *Moisture*-Heat the muffle furnace to 750 °C and place previously ignited porcelain crucibles and covers in the furnace for 10 min. Cool the crucibles in a desiccator for 1 h. 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 h. Place the dried samples in a desiccator for 1 h.
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 open, 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). Then move the samples to the rear 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. Cool the samples in a desiccator for 1 h and weigh.
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 h. Cool the crucibles with lids in place in a desiccator for 1 h and weigh. Repeat burning of the sample until a succeeding 1 h period of heating results in a loss of less than 0.0005 g.

### Calculation and Report

- Calculate the percentage of moisture in the sample as follows:

$$\text{Moisture, \%} = \frac{(A - B)}{A} \times 100 \quad (\text{A.3-1})$$

where :  $A$  = grams of air-dry sample used

$B$  = grams of sample after drying at 105 °C

- Calculate the percentage of volatile matter in the sample as follows:

$$\text{Volatile-matter, \%} = \frac{(B - C)}{B} \times 100 \quad (\text{A.3-2})$$

where :  $C$  = grams of sample after drying at 950 °C

- Calculate the percentage of ash in the sample as follows:

$$\text{Ash, \%} = \frac{D}{B} \times 100 \quad (\text{A3-3})$$

where :  $D$  = grams of residue

- Report all results to the first decimal place. Values for duplicate determinations should agree within the following:

Constituent Determined	Permissible Differences Between Duplicates, %
Moisture	0.1
Volatile matter	0.5
Ash	0.1

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## APPENDIX A.4

### Determination for Iodine Number (ASTM D4607)

#### Procedure

1. Crush and sieve the activated carbon in the size ranged between mesh number 325 (0.045 mm) and 100 (0.150 mm)
2. Dry in an oven at 105°C for 4 h and cool to room temperature
3. Determine of iodine number requires an estimation of three carbon dosages
4. Weigh three appropriate amounts of activated carbon
5. Transfer to 250 ml Erlenmeyer flask equipped with a ground glass stopper
6. Pipet 10.0 mL of 5 wt % hydrochloric acid solution into each flask containing carbon
7. Stopper each flask and swirl gently until the carbon is completely wetted
8. Loose the stoppers to vent the flasks
9. Place on a hot plate in a fume hood
10. Boil gently for  $30 \pm 2$  s
11. Remove the flasks from the hot plate and cool to room temperature
12. Pipet 100.0 mL of 0.100 N iodine solutions into each flask
13. Stopper the flasks, and shake vigorously for  $30 \pm 1$  s
14. Filter each mixture through filter paper (Whatman No. 42) into a beaker
15. Pipet 50 mL of each filtrate into a clean 250 mL Erlenmeyer flask
16. Titrate each with standardized 0.100 N sodium thiosulfate solutions until the solution is a pale yellow
17. Add 2 mL of the starch indicator solution
18. Continue the filtration with sodium thiosulfate until one drop produces a colorless solution
19. Record the volume of sodium thiosulfate used

**Calculation of iodine number (X/M) (mg/g)**

$$X / M = \frac{[A - (DF)(B)(S)]}{M} \quad (\text{A.4-1})$$

where S is sodium thiosulfate volume (mL), M the weight of carbon (g).

To calculate the value of X/M, first device the following value:

$$A = (N_2)(12693.0) \quad (\text{A.4-2})$$

where  $N_2$  is iodine concentration (N).

$$B = (N_1)(126.93) \quad (\text{A.4-3})$$

where  $N_1$  is sodium thiosulfate concentration (N).

$$DF = \frac{[I + H]}{F} \quad (\text{A.4-4})$$

where DF is dilution factor, I iodine volume (mL), H hydrochloric acid volume (mL) and F filtrate volume (mL).

- *Calculation of carbon dosage (M) (g) for calculation iodine number, Eq. (A.4-1)*

$$M = \frac{[A - (DF)(C)(126.93)(50)]}{E} \quad (\text{A.4-5})$$

where C is residual filtrate (N) and E estimated iodine number of the carbon. For approximation carbon dosage (M) may be use Table A.4-1

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Table A.4-1 Approximation carbon dosage (M)

M				M			
E	C=0.01	C=0.02	C=0.03	E	C=0.01	C=0.02	C=0.03
300	3.766	3.300	2,835	1550	0.729	0.639	0.549
350	3.228	2.829	2.430	1600	0.706	0.619	0.531
400	2.824	2.475	2.126	1650	0.684	0.600	0.515
450	2.510	2.200	1.890	1700	0.664	0.582	0.500
500	2.259	1.980	1.701	1750	0.645	0.566	0.486
550	2.054	1.800	1.546	1800	0.628	0.550	0.472
600	1.883	1.650	1.417	1850	0.610	0.535	0.460
650	1.738	1.523	1.308	1900	0.594	0.521	0.447
700	1.614	1.414	1.215	1950	0.579	0.508	0.436
750	1.506	1.320	1.134	2000	0.565	0.495	0.425
800	1.412	1.237	1.063	2050	0.551	0.483	0.415
1000	1.130	0.990	0.850	2250	0.502	0.440	0.378
1050	1.076	0.943	0.810	2300	0.491	0.430	0.370
1100	1.027	0.900	0.773	2350	0.481	0.421	0.362
1150	0.982	0.861	0.739	2400	0.471	0.412	0.354
1200	0.941	0.792	0.680	2450	0.461	0.404	0.347
1250	0.904	0.792	0.680	2500	0.452	0.396	0.340
1300	0.869	0.761	0.654	2550	0.443	0.388	0.333

M				M			
E	C=0.01	C=0.02	C=0.03	E	C=0.01	C=0.02	C=0.03
1350	0.837	0.733	0.630	2600	0.434	0.381	0.327
1400	0.807	0.707	0.607	2650	0.426	0.374	0.321
1450	0.799	0.683	0.586	2700	0.418	0.367	0.315
1500	0.753	0.666	0.567	2750	0.411	0.360	0.309

- Calculation of residual filtrate (C) (N) for calculation iodine number, Eq. (A.4-5)

$$C = \frac{(N_1 \cdot S)}{F} \quad (\text{A.4-6})$$

Using logarithmic paper, plot X/M versus C 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 greater than 0.995.

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## APPENDIX A.5

### Determination for Moisture Content (ASTM D 2867-95)

#### 1). Oven-Drying Method

##### Apparatus

- *Moisture Oven*-Most commercial, electrically heated, forced-circulation drying ovens capable of temperature regulation between 145 °C and 155 °C may be used
- *Capsules with Covers*-Low form glass weighing bottles with ground-glass stoppers or seamless metal boxes with covers may be used. They should be as shallow as possible, consistent with convenient handling
- *Desiccator*

##### Materials

- *Desiccant*-Anhydrous calcium chloride or other suitable desiccant

##### 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 representative sample. Put this into a predried tared capsule with lid, close and weigh 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 °C to 155 °C). Close the oven and dry to constant weight (3 h normally sufficient). Open the oven and cover the capsule quickly. Cool in a desiccator to ambient temperature and weigh.

##### Procedure for Activated Carbon Larger than A No. 50 Sieve

- Use a 5 to 10 g representative sample and weigh to the nearest 2 mg. complete the determination as described in above.

### Calculation

- Calculate the moisture content as follows:

$$\text{Moisture, weight\%} = \frac{(C - D)}{(C - B)} \times 100 \quad (\text{A.5-1})$$

- where :
- $B$  = weight of capsule with cover, g
  - $C$  = weight of capsule with cover plus original sample, g
  - $D$  = weight of capsule with cover plus dried sample, g

## 2). Xylene-Extraction Method

### Apparatus

- *Boiling Flask*-A 300 mL flat-bottom Erlenmeyer flask with ground-glass joints
- *Condenser*-A 300 mL water-cooled condenser of the Allihn type with ground-glass joints
- *Drying Tube*, containing a suitable desiccant with fiber-glass filter
- *Water Trap*-A Bidwell and Sterling 10 mL or a Dean and Stark receiver with ground-glass joints. The water trap should be clean so that the shape of the meniscus at the end of the test is the same as at the beginning
- *Hot Plate*-An electrically heated hot plate with enclosed elements and temperature control

### Reagent

- Xylene-Reagent grade in accordance with the specifications of the Committee on Analytical Reagents of the American Chemical Society

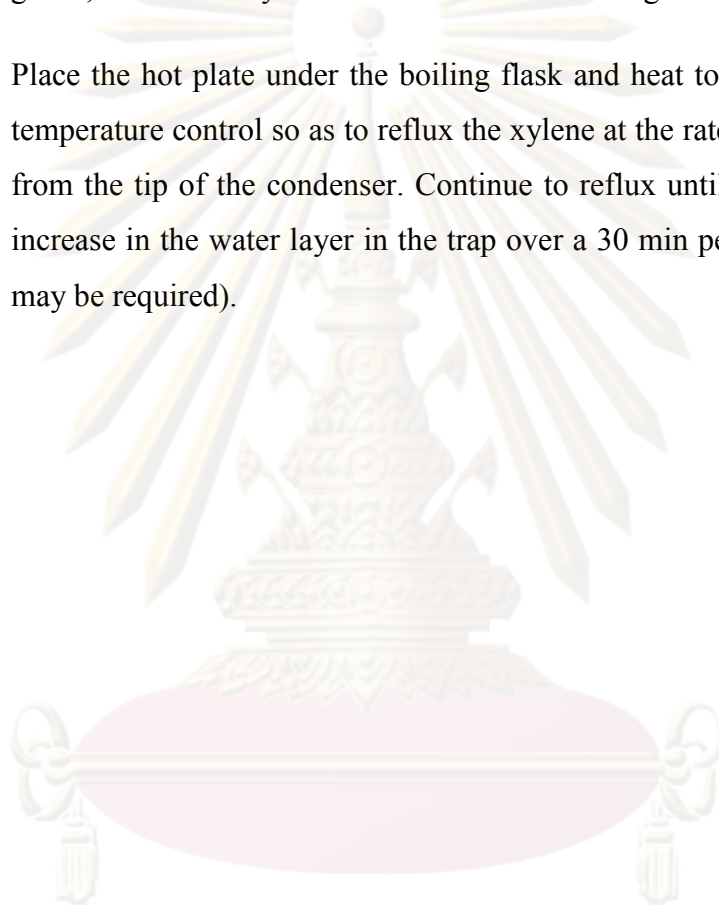
### Preparation of Apparatus

- Clean the condenser, flask, and trap and carefully dry to ensure that it is free of water. Assemble the condenser and water trap



**Procedure**

1. Weigh the sample bottle. Dip out with a spoon from the sample bottle 25 to 50 g of the sample. Put this into the boiling flask and reweigh the sample bottle to the nearest 0.1 g. Add 100 mL of xylene and connect the boiling flask to the water trap. For carbons having density less than 0.30 g/cm<sup>3</sup>, 200 mL of xylene should be used for a 25 g sample.
2. Place the hot plate under the boiling flask and heat to boiling. Adjust the temperature control so as to reflux the xylene at the rate of about 1 drop/s from the tip of the condenser. Continue to reflux until there is no further increase in the water layer in the trap over a 30 min period (from 2 to 8 h may be required).



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## APPENDIX A.6

### Determination for Specific Surface Area (ASTM C 819-77)

#### Apparatus

- Micromeritics, ASAP 2000
- Computer and Program
- Sample tubing

#### Procedure

1. Weigh activated carbon sample size  $8 \times 30$  mesh
2. Dry the activated carbon sample in oven at  $150\text{ }^{\circ}\text{C}$
3. Weigh sample tubing and record
4. Weigh 0.3-0.5 g of activated carbon sample in sample tubing
5. Wash the contaminant molecule on surface area of activated carbon at  $150\text{ }^{\circ}\text{C}$  under vacuum pressure
6. Weigh activated carbon sample and sample tubing after outgas

#### Specific surface area analysis

1. Fix 10 point of relative pressure at equilibrium ( $P/P_0$ )
2. Pass 99.5%  $\text{N}_2$  (free oxygen) until equal to the relative pressure at equilibrium

#### Calculation

- *Determination for specific surface area of activated carbon*

Plot graph between relative pressure ( $P/P_0$ ) and quantities of  $\text{N}_2$  that adsorped at the relative pressure  $[W(P/P_0) - 1] - 1$ , we can calculated the specific surface area by Eq. (A.3-1)

$$S_{BET} (m^2 / g) = \frac{NA_{CS}}{[(S + I)(MW)]} \quad (\text{A.6-1})$$

where :  $N$  = Avogadro number ( $6.02 \times 10^{23}$  molecule/mole)

$A_{CS}$  = Cross section area of  $\text{N}_2$  molecule

$MW$  = Molecular weight of  $\text{N}_2$

## APPENDIX B

**Table B.1 Effect of carbonization temperature and time on physical properties of prepared charcoal**

Carbonization		Yield (%)	Moisture (% by wt)	Volatile matter (% by wt)	Ash (% by wt)	Fixed carbon (% by wt)
Temp. (°C)	Time (min)					
450	30	47.8	1.8	33.0	10.7	48.6
	45	40.4	1.1	29.7	11.5	53.3
	60	40.1	1.0	29.0	12.0	53.4
	90	39.0	1.2	26.4	13.7	56.4
	120	37.3	0.8	25.3	14.1	58.5
500	30	40.3	1.2	28.4	13.4	56.7
	45	37.5	1.4	24.2	14.4	62.4
	60	35.7	0.9	21.7	14.4	66.7
	90	34.8	1.0	19.9	14.6	67.6
	120	34.6	0.9	19.1	16.7	65.9
550	30	36.1	1.1	21.1	14.2	63.4
	45	33.4	1.1	19.8	14.4	64.8
	60	33.6	0.9	15.4	14.4	69.3
	90	32.5	0.8	14.3	14.4	70.3
	120	31.8	0.8	14.0	14.6	71.0
600	30	34.5	1.0	19.8	15.6	64.8
	45	34.4	0.9	19.6	16.0	66.1
	60	33.6	0.8	18.4	16.4	66.4
	90	33.9	0.8	17.3	16.6	67.3
	120	31.8	0.8	15.6	16.9	66.9

**Table B.2 Characteristics of activated carbon form Eucalyptus bark by steam activation**

Activation		Yield (%)	Ash (wt %)	Bulk density (g cm <sup>-3</sup> )	Iodine number (mg g <sup>-1</sup> )
Temperature (°C)	Time (min)				
850	60	75.4	26.6	0.47	308±15
	90	66.3	32.5	0.46	571±57
	120	55.5	35.1	0.41	624±20
900	60	60.4	29.5	0.46	319±29
	90	57.6	32.7	0.39	476±35
	120	52.5	37.3	0.37	693±63
950	60	54.5	30.4	0.41	576±23
	90	53.1	32.7	0.38	604±35
	120	45.1	38.3	0.39	613±53

## APPENDIX C

## Paper Publications (Conference Articles)

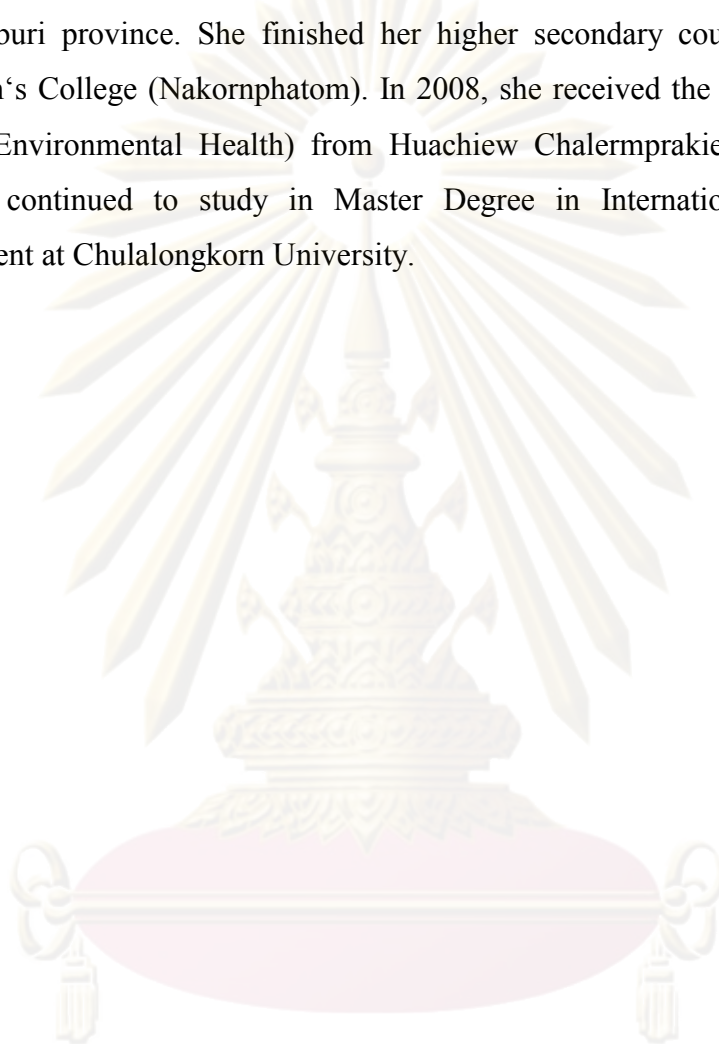
Thanyalak Kiatthanasakun, Vorapot Kanokkantapong, and Prasert Pavasant. **Activated carbon from Eucalyptus bark with carbon dioxide activation**. 2009. The 19<sup>th</sup> Thailand Chemical Engineering and Applied Chemistry Conference October 26-27, 2009, Kanchanaburi, Thailand.



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Miss Thanyalak Kiatthanasakun was born on 19<sup>th</sup> August 1985 in Kanchanaburi province. She finished her higher secondary courses from Princess Sirindhorn's College (Nakornphatom). In 2008, she received the Bachelor Degree in Science (Environmental Health) from Huachiew Chalermprakiet University. After that, she continued to study in Master Degree in International Environmental Management at Chulalongkorn University.



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