การเตรียมถ่านกัมมันต์จากส่วนเหลือใช้ของสบู่ดำ โดยการกระตุ้นด้วย กรดฟอสฟอริก, โพแทสเซียมไฮดรอกไซด์ และ ซิงค์คลอไรด์

นายวิชานนท์ วาสนาทิพย์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

PREPARATION OF ACTIVATED CARBON FROM JATROPHA WASTE VIA PHOSPHORIC ACID, POTASSIUM HYDROXIDE, AND ZINC CHLORIDE ACTIVATIONS

Mr. Wichanon Watsanathip

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2009

Thesis Title	PREPARATION OF ACTIVATED CARBON FROM JATROPHA WASTE VIA PHOSPHORIC ACID, POTASSIUM HYDROXIDE, AND ZINC CHLORIDE ACTIVATIONS
By	Mr. Wichanon Watsanathip
Field of Study	Chemical Engineering
Thesis Advisor	Associate Professor Prasert Pavasant, Ph.D.
Thesis Co-Advisor	Vorapot Kanokkantapong, Ph.D.

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

……………………………………Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing)

THESIS COMMITTEE

……………………………………Chairman
(Associate Professor Muenduen Phisalaphong, Ph.D.)

……………………………………Thesis Advisor
(Associate Professor Prasert Pavasant, Ph.D.)

……………………………………Thesis Co-Advisor
(Vorapot Kanokkantapong, Ph.D.)

……………………………………Examiner
(Associate Professor Deacha Chatsiriwech, Ph.D.)

……………………………………External Examiner
(Assistant Professor Bunyarit Panyapinyopol, Ph.D.)

วิชานนท์ วาสนาทิพย์ : การเตรียมถ่านกัมมันต์จากส่วนเหลือใช้ของสบู่ดำ โดยการกระตุ้นด้วย กรดฟอสฟอริก, โพแทสเซียมไฮดรอกไซด์ และ ซิงค์คลอไรด์. (PREPARATION OF ACTIVATED CARBON FROM JATROPHA WASTE VIA PHOSPHORIC ACID, POTASSIUM HYDROXIDE, AND ZINC CHLORIDE ACTIVATIONS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร.ประเสริฐ ภวสันต์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : ดร. วรพจน์ กนกกันฑพงษ์, 97 หน้า.

การเตรียมถ่านกัมมันต์จากส่วนเหลือใช้ของสบู่ดำ ถูกนำมาทดลองที่ต่างสภาวะ ได้แก่ อุณหภูมิ (500, 600 และ 700 องศาเซลเซียส) เวลาที่ใช้ในการกระตุ้น (60, 120 และ 180 นาที) และอัตราส่วนในการเคลือบฝัง ระหว่าง วัตถุดิบกับสารเคมี (1:0.5 ถึง 1:2) โดยถ่านกัมมันต์ที่ได้จะถูกวิเคราะห์เพื่อที่จะหา พื้นที่ผิวจำเพาะ, ไอโอดีนนัมเบอร์, ขนาดรูพรุนเฉลี่ย, ไอโอดีนนัมเบอร์สุทธิ, พื้นที่ผิวสุทธิ, ความหนาแน่นรวม, เปอร์เซ็นต์ผลได้, หมู่ฟังก์ชัน, และสิ่งเจอปน สภาวะที่ดีที่สุดในการผลิตถ่านกัมมันต์ จากการเตรียมกากและเปลือกสบู่ดำโดยการกระตุ้นโดยโพแทสเซียมไฮดรอกไซด์เกิดขึ้นที่อุณหภูมิ 700 องศาเซลเซียส (ทั้งกากและเปลือก) 180 นาทีสำหรับกาก และ 60 นาทีสำหรับเปลือก และอัตราส่วนในการเคลือบฝัง 1:0.75 สำหรับกาก และ 1:0.5 สำหรับเปลือก ทำให้ได้ค่าพื้นที่ผิว 666 และ 699 ตารางเมตรต่อกรัมถ่านกัมมันต์ และ ไอโอดีนนัมเบอร์ 696 และ 631 มิลลิกรัมต่อกรัมถ่านกัมมันต์ สำหรับกากและเปลือก ตามลำดับ ขนาดรูพรุนเฉลี่ยของถ่านกัมมันต์จากเปลือกสบู่ดำถูกกระตุ้นด้วยซิงค์คลอไรด์ มีขนาดที่ใหญ่ที่สุดที่ 9.86 นาโนเมตร โครงส้ร้างของถ่านกัมมันต์ส่วนใหญ่จะเป็นแบบอสัณฐาน ซึ่งถ่านกัมมันต์ที่กระตุ้นด้วยซิงค์คลอไรด์อาจจะมีผลึกของ ซิงค์ออกไซด์ และ ซิงค์ทูไฮดรอกไซด์คลอไรด์บนผิวของถ่าน ผิวของถ่านกัมมันต์อาจจะมีหมู่ฟังก์ชันหลากหลาย อย่างเช่น หมู่อะโรมาติกส์, หมู่ฟังก์ชันที่มีวงเบนซีน และหมู่ไฮดรอกซิล เมื่อนำเอาค่าเปอร์เซ็นต์ของผลได้นำเข้าไปคิดพิจารณาร่วมกับสภาวะที่ดีที่สุดของการผลิตถ่านกัมมันต์ ซึ่งใช้กากสบู่ดำเป็นวัตถุดิบ และใช้ซิงค์คลอไรด์เป็นสารกระตุ้น ซึ่งค่าผลได้มีค่าสูงอยู่ที่ 64 กรัมถ่านกัมมันต์ต่อกรัมวัตถุดิบ

ภาควิชา..............วิศวกรรมเคมี..........ลายมือชื่อนิสิต..
สาขาวิชา...........วิศวกรรมเคมี..........ลายมือชื่อ อ. ที่ปรึกษาวิทยานิพนธ์หลัก..................
ปีการศึกษา.........2552......................ลายมือชื่อ อ. ที่ปรึกษาวิทยานิพนธ์ร่วม..................

5170622321 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: ACTIVATED CARBON/ JATROPHA SEED CAKE/ JATROPHA SHELL/ ZINC CHLORIDE/ PHOSPHORIC ACID/ POTASSIUM HYDROXIDE

WICHANON WATSANATHIP: PREPARATION OF ACTIVATED CARBON FROM JATROPHA WASTE VIA PHOSPHORIC ACID, POTASSIUM HYDROXIDE, AND ZINC CHLORIDE ACTIVATIONS. THESIS ADVISOR: ASSOC. PROF. PRASERT PAVASANT, Ph.D., THESIS CO-ADVISOR: VORAPOT KANOKKANTAPONG, Ph.D., 97 pp.

The preparation conditions of activated carbon from waste of jatropha were determined at various temperatures (500, 600, and 700°C), activation times (60, 120, and 180 min.), and ratios of raw material:chemical agent (1:0.5 – 1:2). The derived activated carbon was analyzed for its specific surface area, iodine number, average pore size, net iodine number, net surface area, bulk density, %yield, functional groups, and purity. The best conditions for the production of high surface area of activated carbon from jatropha seed cake and shell were the activation with potassium hydroxide at the activation temperature of 700°C (for both cake and shell), activation time of 180 (cake) and 60 (shell) minutes, and impregnation ratio of 1:0.75 (cake) and 1:0.5 (shell). At this optimal condition, the BET surface areas were 666 and 699 m^2/g, and iodine numbers were 696 and 631 mg/g for seed cake and shell, respectively. The average pore size of activated carbon from jatropha shell with zinc chloride was the largest, at 9.86 nm. The structure of activated carbon were mainly amorphous, where the activated carbon with zinc chloride might contain the crystals of ZnO and $Zn_5(OH)_8Cl_2 \cdot H_2O$ on the carbon surface. The surface of activated carbon might contain several functional groups including aromatic, benzene derivatives, and hydroxyl groups. When %yield was included in the consideration, the best combination for the production of activated carbon was to use jatropha seed cake as a raw material, and zinc chloride as activating agent as this provided the yield at as high as 0.64 g activated carbon/g raw material.

Department :…….Chemical Engineering……......Student's Signature……………......
Field of Study :......Chemical Engineering…...….Advisor's Signature……………..
Academic Year :...2009………………...……...Co.Advisor's Signature……………

ACKNOWLEDGEMENTS

This thesis will never have been completed without the help and support of many people and organizers who are gratefully acknowledged here.

Firstly, I would like to express my sincere gratitude to Associate Professor Prasert Pavasant, my advisor, for his suggestions, guidance, warm encouragement, excellent and generous supervision throughout my master program.

Secondly, I would like to thank Dr. Vorapot Kanokkantapong who is an thesis co-advisor for their valuable suggestions, guidance, warm encouragement and generous supervision throughout my master program. I am grateful to Associate Professor Dr. Muenduen Phisalaphong, chairman of the committee, Associate Professor Dr. Deacha Chatsiriwech, and Assistant Professor Bunyarit Panyapinyophol, members of the committees for many valuable suggestions. In addition, I would also like to thank Assistant Professor Dr.Worapon Kiatkittipong who is an my advisor in Bachelor Degree of Engineering (from Silpakorn University) for his valuable recommendation me to continually study in the Master Degree and influent me to meet the best advisor, Associate Professor Dr. Prasert Pavasant.

This study, the jatropha seed cake and shell that was used to produce the powder activated carbon were provided by Jatropha school, Kasetsart University Kamphaeng Saen Campus, Nakornpathom province, Thailand.

Moreover, my work could not have been carried out without the help of colleague, Akekasit Eiadpum supported the informations and analyzed the samples with UV/VIS Spectophotometer, Uraiwan Phongsa supported the information and analyzed the samples with FTIR. Moreover, special thanks should be made for all members in the Environmental and Biochemical Engineering Laboratories for their pleasantness and encouragement. I would also like to thank P'Max, P'Big, P'Muay, P'Toey, P'Tik, Aom, and Aim for kind of help of them. Moreover, special thanks should be made for the Graduate School, Chulalongkorn University to giving the place as warm home for two years of my Master Degree research.

I would like to express love and thanks to my family (my father, my sister, my brother) supports that have propelled me to the completion of this work and worthy supports at all times for their worth supports throughout my Master course.

CONTENTS

Page

Page

LIST OF TABLES

Page

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Motivations

Energy crisis is currently one of the most significant global problems, and the seek for alternative energy sources has been set out as an international target for which considerable research efforts have been invested. Agricultural sources have been proposed as potential options as they are generally renewable and exert a lower impact on the release of greenhouse gases such as carbon dioxide to the atmosphere when compared to fossil fuels. Among the various energy options, biodiesel has been proposed as one of the most feasible. Biodiesel can be produced from several kinds of raw materials such as coconut oil, palm oil, etc. Jatropha is one of the promising plants for serving the biodiesel production because of its durability to the drought of countries within equator region, including Thailand. Extraction oil from Jatropha seed can be used directly in diesel engines where four kilograms of Jatropha seed could generate approx. one liter of oil, during the biodiesel production, a large quantity of waste from Jatropha seed cake is produced and being a problem to eradicate.

Generally, agriculture waste is converted to energy, or fermented in order to produce biogas and fertilizer. Jatropha wastes are no exception, and these can be effectively further processed to fertilizer due to their high nitrogen content. However, this option does not provide value-adding to the wastes as organic fertilizer could, at best, cost at only 10 baht per kilogram.

Activated carbon is one of the favorable treatment approaches using adsorption mechanism. It involves not only in several industrial sectors e.g., air purifier industry, drinking water and tap water industry, metal-plated industry, and food industry, but in domestic sector purposes also, e.g. absorbing odors from refrigerator, wardrobe and closet’s smells, etc. Rate of activated carbon imported from the United State, Japan, Malaysia, and Indonesia to Thailand in the years 2005 to 2008 has continuously increased from 205, 267, 729 and, 1,230 million baht, respectively. Thus, it can be seen that activated carbon market is wide and has potential for consistent demand in the country. It should be conclusively stated that activated carbon can mainly be generated from agriculture waste. The cost of activated carbon is normally over 3 times comparing to fertilizer. Hence, this study aims to investigate the conversion of jatropha seed cake to activated carbon using chemical treatment. This is a preliminary examination to evaluate the possibility in such conversion.

1.2 Objectives

This main objective of this work is to generate the activated carbon from Jatropha by chemical activation.

- Find optimal conditions in the production of activated carbon from jatropha seed cake and shell by chemical activation.

1.3 Scopes of the research

1.3.1 The determination of optimum conditions for the activation of Jatropha from each part is performed by varying the following parameters:

- Activation temperature in range 400 – 700°C
- Weight ratio of raw material and chemical reagent (impregnation ratio): 1:0.5 – 1:2
- Activation time: 0.5 - 3 hours
- Chemical agent: phosphoric acid, potassium hydroxide and zinc chloride

1.3.2 Properties of activated carbon are indicated by:

- % yield
- % volatile matter
- % ash content
- % fixed carbon
- Apparent (bulk) density
- Iodine number
- Specific surface area (BET method)
- Fourier transform infrared (FTIR)
- X-ray diffraction (XRD)
- Ultimate analysis (CHNS/O)

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Jatropha

Jatropha curcas L. (Figure 2.1) is a native plant in South America. It has a long history of propagation in Africa and Asia by Portuguese. (Bringi, 1987) Jatropha curcas L. or ‘‘physic nuts,’’ which will be called ‘‘Jatropha’’ below, is a small tree or large shrub that normally reaches a height of 3–5 meters, but can reach a height of 8–10 meters under favorable conditions. (Carels et al., 2009) The productive lifespan of Jatropha is around 50 years. Jatropha produces first time fruit after 6 months and the productivity is stable after 1–3 years old. (Manurung and Satyawati, 2006) Jatropha can be used as traditional medicine and being an essential renewable energy source. The physical properties of jatropha fruit depend on its moisture content, and this knowledge is essential for the design of harvest and post harvest equipments (e.g., mechanical harvesters, driers, graders, decorticators, and storage bins). (Sahay, 1996) Jatropha oil, produced from seed (Figure 2.2), can be utilized to produce biodiesel fuel by esterification reaction with short chain alcohols, preferably at their super critical conditions without the use of catalysts. (Hawash et al., 2009) This biodiesel from Jatropha can be used in direct or indirect diesel engines, piston ring, and fuel injector choking. As the result, many Jatropha seed cakes (Figure 2.3) are generated as byproduct. Generally, Jatropha produces approx. 1 ton of both of seed cake and shell per 10,000 m^2. A large amount of this seed cake waste will be a huge problem in the near future. The method to manage jatropha seed cake currently is fermented for fertilizer and biogas production. Some researchers investigated seed cake as a substrate for the industrial production of enzymes such as proteases and lipases. (Carels et al., 2009)

Figure 2.1 Jatropha curcas L.

Figure 2.2 Jatropha seed

Figure 2.3 Jatropha seed cakes

2.2 Activated carbon

There are many definitions of an activated carbon and the favorite one is “a material prepared to exhibit a high degree of porosity and an extended inert-particulate surface area”. (Haimour and Emeish, 2006) Activated carbon is of interest in many industries such as food processing, pharmaceuticals, chemical, petroleum, and nuclear. It is produced from several types of agriculture materials. Two main factors to consider agriculture materials as favorite raw material because they are renewable sources and low cost. (Gurses et al., 2006) The samples of raw material are hazelnut shell (Aygun et al., 2003) rice-husk (Daifullah et al., 2004) rubber wood sawdust (Srinivasakannan et al., 2004) coconut shell (Gratuito et al., 2008) palm stems (Jibril et al., 2008) eucalyptus dehn bark (Patnukao and Pavasant, 2008) coffee husk (Oliveira et al., 2009) and soybean oil cake (Tay et al., 2009). The considered properties of raw materials for the production of activated carbon are

(i) low organic volatile content because volatiles are more released at higher temperature resulting in the lower % yield (Aravindhan et al., 2009)
(ii) inexpensive raw materials (Youssef et al., 2005)
(iii) low ash content in raw material because of higher yield for final product which is mainly carbonaceous in nature
(iv) high and stable properties for long life
(v) high carbon fixed content which is essential for producing highly porous materials. (Lua et al., 2004)

Proximate analysis of various raw materials shown in Table 2.1.

Table 2.1 Proximate analysis of various raw materials

Raw materials	Moisture (%)	Volatile (%)	Ash (%)	Fixed carbon content (%)	Reference
Pistachio-nut shells	4.0	73.4	1.0	21.6	(Lua et al., 2004)
Rubber wood sawdust	6.2	69.7	0.8	23.4	(Srinivasakannan et al., 2004)
Sugarcane bagasse	6.1	65.9	3.3	24.7	(Kalderis et al., 2008)
Jackfruit peels	10	50.0	4	36.0	(Prahas et al., 2008)
Seaweeds	8.8	51.7	5.2	34.5	(Aravindhan et al., 2009)
Coconut shell	10.5	78.3	0.8	21.0	(Li et al., 2009)

2.3 Types of activated carbon

There are three main forms of activated carbon. (Gurses et al., 2006)

2.3.1 Powdered activated carbon (PAC)

Powdered forms are the type of activated carbon where small pores and large internal surface area are the main features. (Usmani et al., 1994) After activation, carbon is pulverized to a suitable size normally in the range less than 0.18 mm (US Mesh 80). These are mainly used in liquid phase applications and for flue gas treatments.

2.3.2 Granular activated carbon (GAC)

GAC has larger particle size compared to powdered activated carbon. It is produced by grinding the raw material, adding suitable binders for hardness, re-compacting, and crushing to the required mesh size. The advantages of GAC application are low pressure drop in column and high-efficiency purification of liquids. This type is used in both liquid and gas phase applications.

2.3.3 Pellets or extruded activated carbon (EAC)

EAC is one type of activated carbon with diameter 0.8-4.5 mm and cylindrical shaped. The production is the same as that of granular form. EAC is mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

2.4 Production of activated carbon

The production process of activated carbon can be divided into three steps. (Srinivasakannan et al., 2004)

2.4.1 Dehydration

Dehydration is a process for drying, remove moisture, and dehydrate agents such as sulphuric acid, phosphoric acid

2.4.2 Carbonization

Carbonization or pyrolysis is a process that aims to increase carbon ratio of the material. The process can be achieved in the absence air at temperature lower than 700 ^{o}C. During the process, organic substance in raw material has been converted to carbon and the volatile compounds are removed. There are three steps of the carbonization process:

(i) Dehydration of raw material under temperature range from 27-197 ^{o}C,

(ii) Remove pyrolysis products such as gas and tar oils in the structure under the temperature range from 197-497 °C, and

(iii) Formation of char structure lowering the density of the material under the temperature range from 497-847 °C.

2.4.3 Activation

Activation is a process that targets for increasing surface area and pore of activated carbon which can enhance the ability of adsorption. The type and degree of activation process affect its physical and chemical properties as follows:

(i) Physical or gas activation

Physical activation processes with steam, nitrogen or carbon dioxide are used for mild oxidation of the carbonaceous matter. (Namasivayam et al., 2007) The process is usually carried out in two stages i.e., carbonization and activation stage. (Haimour and Emeish, 2006) Raw material is primary process in physical carbonization by pyrolyzed at temperature range of 600-900^{o}C in absence air and consequently physical activation process by carbonized with oxidizing atmosphere at temperature usually range from 600-1,200^{o}C.

(ii) Chemical activation.

Chemical activation usually uses chemical agents to impregnate raw material at range of temperature 450-900^{o}C. The activated carbons obtained by chemical activation are with high surface area and with well-developed microporosity, which can be controlled and maintained narrow. (Budinova et al., 2008) In chemical activation processes, all chemical agents used are dehydrating agents that influence pyrolytic decomposition and inhibit formation or tar, thus, enhancing the yield of carbon. (Aravindhan et al.,2009) The most widely chemical used is acid such as phosphoric acid (H_3PO_4) (Srinivasakannan et al., 2004; Temmink and Grolle, 2005; Haimour and Emeish, 2006; Patnukao and Pavasant, 2008; Daifullah et al., 2004; Baccar et al., 2009; Gratuito et al., 2008; Jibril et al., 2008; Kalderis et al., 2008; Prahas et al., 2008; Yagmur et al., 2008; Rosas et al., 2009), and etc., base such as potassium carbonate (K_2CO_3) (Budinova et al., 2008; Cabal et al., 2009; Tay et al., 2009), potassium hydroxide (KOH) (Jibril et al., 2008; Wang et al., 2008; Sutcu and Demiral, 2009), and etc. and salt such as sodium chloride (NaCl) and zinc chloride ($ZnCl_2$). (Aygun et al., 2003; Gurses et al., 2006; Aravindhan et al., 2009; Alhamed et al., 2009; Olivares-Marin et al., 2009; Oliveira et al., 2009) However, phosphoric acid is the most preferred because of the less corrosion problem, inefficient chemical recovery, and environmental disadvantages compared to zinc chloride. (Diao et al., 2002; Oliveira et al., 2009)

The advantages of the chemical activation compared to physical activation are lower activation temperature and shorter treatment time. Moreover, activated carbon prepared from chemical activation process often introduces large surface area and well-developed microporosity as shown in Table 2.2.

Table 2.2 Advantages and disadvantages of physical and chemical activations (Budinova et al., 2006)

	Chemical activation	Physical activation
Advantages	- higher yield - larger surface area - lower operating cost - lower energy cost - suitable pore size - lower temperature of activation - good porous structure	- lower contaminant - no activating agent waste
Disadvantages	- contaminant with hazard chemical - impurities from activating agent	- lower yield - high temperature requirement

2.5 Phosphoric acid activation

Phosphoric acid has been mostly used for the activation of lignocellulosic materials. (Srinivasakannan et al., 2004) The process of using phosphoric acid to produce activated carbons is obtained at low temperature (450–600°C) and presents a wide opened micro-pore structure with an important contribution of mesopores. (Martin-Gullon et al., 2004) The activated carbons treated with phosphoric acid, normally, exhibit higher adsorption capacity than those treated with zinc chloride. This is because of the strong dehydration affinity of phosphoric, which leads to a greater surface area and hence greater adsorptive capacity. (Haimour and Emeish, 2006) For higher concentration of phosphoric acid, the development of microporosity is negligible. The main development corresponds to mesoporosity which higher than micropore volume. (Marsh and Rodriguez-Reinoso, 2006) The acid activation likely results in generation of several o-functional groups (e.g. carboxylic, phenolic, and lactones). (Girgis et al., 2009) The reaction between carbon and phosphoric acid at high temperature are develops more pores and P_4 (phosphorus gas), which in condition gas, CO_2, H_2O and other volatile materials. The mechanism was suggested as follows: (Jibril et al., 2008)

$$5C(s) + 2P_2O_5(l) \text{----->} P_4(g) + 5CO_2(g) \tag{2.1}$$

$$2H_2P_2O_7^{2-} \text{------>} P_4(g) + 6O_2(g) + 2H_2O(g) \tag{2.2}$$

Activated carbons prepared with phosphoric acid are useful in the adsorption of hydrocarbons, evaporative emission control from vehicles fuel system, and solvent recovery.

2.6 Potassium hydroxide activation

Potassium hydroxide in carbonization process does not act as a dehydrating agent, but it creates some porosity and produces K_2CO_3 as a by-product (Lillo Rodenas et al., 2003), then KOH is reduced to metallic potassium. (Marsh et al., 1984) Since potassium is intercalated between the graphene layers of structure the carbon particles break down then the carbon particles disintegrate into powder. (Marsh and Rodriguez-Reinoso, 2006) Jibril et al. (2008) studied the effects of H_3PO_4 and KOH in carbonization of lignocellulosic material and revealed that insignificant porosity was occurred at 400^{o}C. At higher temperature, the KOH impregnation seems to develop more pores and wider size distributions over the acid impregnation. El-Hendawy et al. (2009) prepared the activated carbon from maize stalks by KOH activation. It was found that the derived activated carbon reached specific surface area at 1684 m^2/g. The different surface characteristic was mainly located in the micropore area and depended on the KOH concentration. Sutcu and Demiral (2009) produced activated carbon from Loquat stones by KOH and NaOH activations. The results showed that activated carbon activated by KOH produced higher BET surface area compared to NaOH activation. Moreover, the surface area increased from increasing amount of chemical agent affect to decreasing the char size affect to decreasing yield. The reactions of KOH activation are follows: (Jibril et al., 2008)

(1) Formation of K_2CO_3 from KOH: at approx. 400^{o}C

$$4KOH + {=}CH_2 \text{ -----> } K_2CO_3 + K_2O + 3H_2 \qquad (2.3)$$

(2) Reaction of K_2CO_3 with carbon at about 500^{o}C gives CO_2 and intermediate (C-O-K) product that serves as active site for gasification.

(3) Observation of CO at 650^{o}C

$$K_2O + C \text{ -----> } 2K + CO \qquad (2.4)$$

$$K_2CO_3 + 2C \text{ -----> } 2K + 3CO \qquad (2.5)$$

2.7 Zinc chloride activation

Zinc chloride acts as a dehydrating agent that promotes the decomposition of carbonaceous material during the pyrolysis process, restricts the formation of tar, and increases the carbon yield. (Gurses et al., 2006) Activation temperature is usually used in the range of 500-700^{o}C (Alhamed et al., 2009), 400-800^{o}C (Aravindhan et al., 2009), 650^{o}C. (Bestani et al., 2008) From the period literature, the concentration of zinc chloride was used such as, 1100 g of zinc chloride/liter (Mozammel et al., 2002), 14–69 wt% (Nakagawa et al., 2007), 3M $ZnCl_2$ (Gurses et al., 2006), (10, 20, 30, 40, and 50% w/v) (Aravindhan et al., 2009) for this study using 55 wt% $ZnCl_2$ in concentration to zinc chloride activation. The ratio of $ZnCl_2$ to raw material of less than 1.0 and greater than 1.5 resulted in the production of micro- and mesoporous carbons, respectively. (Ucar et al., 2009) Usually treated by mixing acid solution into activated carbon after carbonization to eliminate excess $ZnCl_2$ such as, 0.5 N HCl

(Ganan-Gomez et al., 2006; Aravindhan et al., 2009), 1N HCl (Yorgun et al., 2009), 3 M HCl (Qian et al., 2007) or wash with hot distilled water several times. (Bestani et al., 2008; Ucar et al., 2009) or treated by mixing acid solution follow wash with distilled water.

2.8 Important parameters for activation

2.8.1 Impregnation ratio

For chemical activation, impregnation ratio (raw material weight: chemical agent) is an important parameter that affected %yield, surface area and pore volume of the final product. Impregnation ratio for chemical activation has been generally reported in the range of 1:1 - 1:2. (Baccar et al., 2009; Gratuito et al., 2008; Srinivasakannan et al., 2004) Generally, the yield of carbon decreases as the impregnation ratio increases, because excess agent will promote gasification of char and increases the total weight loss of carbon. (Prahas et al., 2008) Baccar et.al (2009) used olive waste cake as a raw material to produce activated carbon using H_3PO_4 as chemical agents. They found that suitable impregnation ratio occurred at 1:1.75 and this gave the iodine number at approx. 580 mg/g and also showed the best development of microporous structure. Srinivasakannan et.al (2004) performed production of impregnation ratio of 1:1 was as well as ratio 1:2 where the iodine number increased from 842 mg/g at 1:1 to 958 mg/g at 1:2.

2.8.2 Activation temperature

The activation temperature is a vital parameter that controls the activated carbon process such as %yield, pore volume and density. The %yield of carbon decreased with an increase in pyrolysis temperature because more volatiles are released at higher temperature. (Aravindhan et al., 2009; Haimour and Emeish, 2006) An increase in activation temperature also develops micro-pore which enhances the adsorptive capacity. (Baaoui et al., 2001) Furthermore, higher activation temperature can cause a large number of small pore volume, however, the surface area decreases.

2.8.3 Activation time

Activation time is an effective parameter for the development of porous network. Low activation time, although results in high yield, leads to an incomplete burn-off. The activation time should be long enough to eliminate moisture and volatile compounds in the raw material to cause pores to develop. (Gratuito et al., 2008) Extended activation time using H_3PO_4 as a chemical agent has an impact on the nature of internal porosity and adsorptive characteristics of the carbon product. (Girgis et al., 2009) However, in some cases, activation time does not cause significant differences in the characterization on the activated carbon. (Chandra et al., 2009) From the period literature, the minimum activation time was Cabral et al. at 10 min., activation temperature 750^{o}C, the resulting of this experiment was surface area is 1580 m^2/g.

2.9 Functional groups on the surface

The chemically activated carbon after pyrolysis has highest content of carboxylic groups, hydroxyl groups (Yagmur et al., 2008) and phosphorous-containing acidic groups. (Budinova et al., 2006) The acid activation is likely to result in the generation of several o-functional groups (e.g. carboxylic, phenolic, and lactones). (Girgis et al., 2009) On the other hand, the basic activation is likely to result in hydroxyl groups, methyl groups, aromatic ring, C=O (ketones and carboxylic acid), benzene derivative, etc. (El-Hendawy, 2009) In zinc chloride activation, it is quite usual to find oxygenated group, alkyne group, carbonyl group, phenol group but Zn, which metal is not impregnation in activated carbon. (Alhamed et al., 2009)

The mechanism of chemical activation with H_3PO_4 was suggested particularly for the evolution of porosity and the formation of surface functional groups. (Guo and Lua, 2003)

$$C_nH_xO_y + H_3PO_4 \text{ ----> } [C_nH_xO_y\text{-}HPO_3] + H_2O \tag{2.6}$$

For KOH impregnation, the following reaction was proposed to occur during activation process: (Guo and Lua, 2003)

$$C_nH_xO_y + KOH \text{ ----> } [C_nH_{x-1}O_y\text{-}K] + H_2O \tag{2.7}$$

2.10 Structure of activated carbon

Activated carbon is a micro porous inert carbon with a large internal surface. On this surface organic molecules from liquids or gases can adsorb. The basic structural unit of activated carbon is closely approximated by the structure 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 shown in Figure 2.4.

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

Figure 2.4 Structure of activated carbon

2.11 Porous structure of activated carbon

Generally, activated carbons have three types of pore: (i) micro-pore (ii) meso-pore and (iii) macro-pore.

2.11.1 The microporosity is mainly generated by the acid agent remaining in the impregnated material which inhibits the contraction of the material during carbonization. (Daifullah et al., 2004)

2.11.2 The mesoporosity is mainly caused by the hydrolysis of the lignocellulosic material and subsequent partial extraction of some of its components during impregnation. This property can usually be tested with methylene blue adsorption which also serves as a model compound for adsorption of organic contaminants from aqueous solution (Aygun et al., 2003) such as Pb^{2+} ions etc. There are two methods to develop mesoporosity:

(i) The carbonization process itself creates mesoporosity by parent material associated with shrinkage, etc. referred to “indigenous mesoporosity” and

(ii) microporous is “activated physically” from gasification with steam or carbon dioxide, when carbon atoms of carbon structure are gasified leaving “molecular holes” then created mesoporosity. (Marsh and Rodriguez-Reinoso, 2006)

2.11.3 The macroporosity is most commonly used in polymer science and technology, it is reasonable to accept it as the generic name of crosslinked polymers having dry state porosity, irrespective of the size of the pores (Okay, 2000) and application in membrane, and synthesis catalyst.

Porous character of activated carbon shown in Table 2.3 and structure of activated carbon showed Figure 2.5.

Table 2.3 Porous character of activated carbon. (Patnukao and Pavasant, 2008)

	Macropores	Mesopores	Micropores
Diameter of pores	more than 200 nm	between 20-200 nm	less than 20 nm
Specific surface area	less than 0.5 m^2/g	20-100 m^2/g	300-2,500 m^2/g
Volumes of pores	0.2-0.8 cm^3/g	limits 0.1-0.5 cm^3/g	0.2-0.6 cm^3/g
Transportation			adsorption proceeds using the mechanism of volume filling

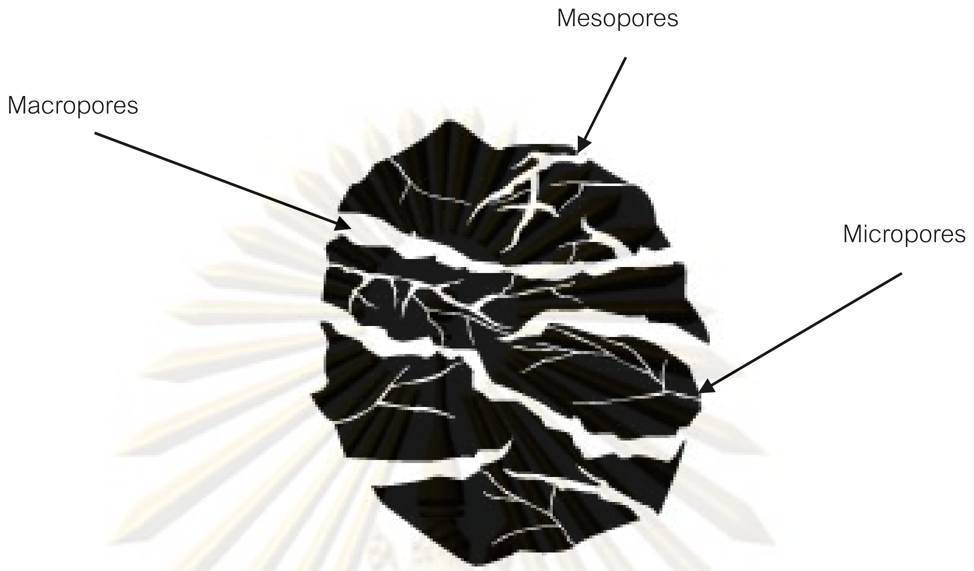

Figure 2.5 Porous character of activated carbon

2.12 Activated carbon properties analysis

Characteristic of activated carbon can be analyzed by many processes such as adsorption ability using iodine number or methylene blue testing, surface area using Brunauer, Emmet and Teller (BET), functional group region surface using Fourier Transform Infrared Spectroscopy (FTIR), the ultimate analysis performed in CHNS/O analyzer, and surface morphology of activated carbon visualized via scanning electron microscopy (SEM).

2.12.1 Ash content

Ash content of activated carbon is inorganic which inertness and amorphism. Generally, good activated carbon should have low ash content. Ash content can be measure following ASTM D2866-94.

2.12.2 BET-surface area

Preference internal surface area of activated carbon normally measures by a method developed by Brunauer, Emmett & Teller which setting up the adsorption-isotherms of liquid nitrogen at -196 °C. The BET-surface can reach up to 1200 m^2/g (average 1000 m^2/g for a high quality).

2.12.3 Density

Density of the activated carbon is the carbon weight (kg) per 1 liter. The value ranges from 300 to 500 g/l depending on the raw materials. A simple calculation for determining the volume activity of activated carbon is to multiply the bulk density by the Iodine Number.

2.12.4 Iodine number

Iodine number is determination of relative activation level of unused or relativated carbons by adsorption of iodine from aqueous solution. The amount of iodine absorbed (in milligrams) by 1 g of carbon using test conditions listed here is called the iodine number. Iodine number can be measure following ASTM D4607-94.

2.12.5 Moisture content

This is the amount of water on the activated carbon under normal condition. A high moisture content indicates poor quality and a normal value varies between 1-5%. Moisture content of activated carbon can be measure following ASTM D2867-04.

2.12.6 Ultimate analysis

Ultimate analysis of raw material can be performed by CHNS/O analyzer using gaseous products feed by pyrolysis in high purity oxygen and are chromatographically detected with a thermal conductivity detector. is developed following ASTM standards for chemical analysis of wood charcoal (ASTM D 1762-84).

2.12.8 Chemical analysis of wood charcoal

Chemical analysis of wood charcoal can examine according to the standard method ASTM D 1762-84.

2.12.9 Fourier Transform Infrared Spectrophotometer (FTIR) analysis

The activated carbon samples are brought to constant weight in a drying oven at 50ºC for 24 h and kept in the desiccators. Then 1 mg of dried granular activated carbon is mixed with 100 mg of KBr, which is initially dried at 110ºC, in the sample disk. FTIR spectra in the range of 450-4000 cm^{-1} were obtained on a Perkin-Elmer, Model 1760X.

2.12.10 X-ray diffraction (XRD) patterns

X-ray diffraction (XRD) patterns obtains by a X-ray Diffraction Spectroscopy using Cu $K\alpha$ radiation (λ=0.154056 nm) with a step size of 0.004° and a step time of 1.5 s.

2.12.11 Surface morphology

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

2.13 Literature review

Activated carbon is most widely produced from agricultural waste such as coconut shell, eucalyptus bark, hazelnut shell, rubber wood, rice-husk, palm stems, coffee husk, soybean oil cake, and coconut shell as this is generally low cost, using renewable source, and is one way of enhancing waste value. Activated carbons are generally produced using two activation methods. The first method is the physical or gas activation (Savova et al., 2001; Lua et al., 2004; Namasivayam et al., 2007; Ncibi et al., 2009), using steam, nitrogen, and carbon dioxide at high temperature in order to increase adsorptive capacity and surface area. This physical means usually involves two steps: carbonization and activation. Recent research, Savova et al. (2001) used steam activation to convert almond shell to activated carbon. The condition was: carbonization temperature 800^{o}C 60 minutes, activation temperature 800^{o}C 60 minutes. The resulting activated carbon had the surface area of 998 m^2/g. Recent works on the production of activated carbon with physical activation are demonstrated in Table 2.5. The second method is the chemical activation, using chemical agent to activate raw material in order to produce activated carbon with high surface area and high adsorptive capacity. Chemical agents most widely used can be categorized into three types: (i) acid such as phosphoric acid (H_3PO_4) (Srinivasakannan et al., 2004;

Daifullah et al.,2004; Temmink and Grolle, 2005; Haimour and Emeish, 2006; Patnukao and Pavasant, 2008; Demirbas, 2008; Gratuito et al., 2008; Jibril et al., 2008; Yagmur et al., 2008; Baccar et al., 2009; Rosas et al., 2009), hydrochloric acid (HCl), and sulfuric acid (H_2SO_4) Demirbas, 2008 (ii) base such as sodium hydroxide (NaOH), potassium hydroxide (KOH) (Jibril et al., 2008; Wang et al., 2008; El-Hendawy, 2009), and potassium carbonate (K_2CO_3) (Budinova et al., 2008 ; Cabal et al., 2009 ;Tay et al., 2009) (iii) salt such as zinc chloride ($ZnCl_2$). (Aygun et al., 2003; Gurses et al., 2006; Kalderis et al., 2008; Alhamed et al., 2009; Aravindhan et al., 2009; Olivares-Marin et al., 2006; Oliveira et al., 2009) In case of phosphoric acid as chemical agent, Srinivasakannan et al. (2009) used phosphoric acid activation to convert rubber wood sawdust to activated carbon using the best condition at 500^oC and 45 min. The resulting iodine number was 1096 mg/g and the surface area of 1496 m^2/g. Sutcu and Demiral et al. (2009) used potassium hydroxide activation to loquat stones convert to activated carbon, with the following conditions: activation temperature 1000^oC and 120 min. The activated carbon had the surface area of 2915 m^2/g. A successful example of using salt as chemical agent can be seen from the work of Olivares-Marin et al. who employed zinc chloride to convert cherry stone to activated carbon with the activation temperature of 550^oC at 120 min. The resulting activated carbon had the surface area of as much as 1971 m^2/g. In summary, chemical agents that require low activation temperature can be ordered according to its superiority as: zinc chloride, phosphoric acid, and potassium hydroxide, whereas the order of chemical agents which reduce the activation time is phosphoric acid, potassium hydroxide, and zinc chloride. Some recent works on the production of activated carbon with chemical activation are given in Table 2.4.

Table 2.4 Recent works on the production of activated carbon with chemical activation

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Hazelnut shell	Chemical/$ZnCl_2$				800	120	965	793	(Aygun et al., 2003)
Rubber wood sawdust	Chemical/H_3PO_4	1:1.5			500	45	1,096	1,496	(Srinivasakannan et al., 2004)
Rice-husk	Chemical/H_3PO_4	1:0.7			500	150		376	(Daifullah et al., 2004)
Wastewater (papper)	Chemical/H_3PO_4							1,400	(Temmink and Grolle, 2005)
Rosa canina fruits	Chemical/$ZnCl_2$	1:5			500	60	495	800	(Gurses et al., 2006)
Date stone wastes	Chemical/H_3PO_4	1:0.4	RT	1440	800	60	495		(Haimour and Emeish, 2006)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Eucalyptus dehn bark	Chemical/H_3PO_4	1:1			500	60	1,043	1,239	(Patnukao and Pavasant, 2008)
Antibiotic production	Chemical/K_2CO_3	1:1	60	120	900	120	1,170	1,260	(Budinova et al., 2008)
Hazelnut shell	Chemical/H_2SO_4				200	1440	204	441	(Demirbas, 2008)
Coconut shell	Chemical/H_3PO_4	1:1.725	RT	720	416	19.5		1,151	(Gratuito et al., 2008)
Palm stems	H_3PO_4		85	180	500	120		1,100	(Jibril et al., 2008)
	KOH				600	120		947	
Sugarcane bagasse	Chemical/$ZnCl_2$	1:0.75	150	1440	700	30		674	(Kalderis et al., 2008)
Rice husk	Chemical/$ZnCl_2$	1:1	150	1440	700	30		750	(Kalderis et al., 2008)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Jackfruit peel waste	Chemical/H_3PO_4			1440	550			1,260	(Prahas et al., 2008)
Activated sludge	Chemical/KOH	1:2.5	RT	1440	600	60	563	382	(Wang et al., 2008)
Waste tea	Chemical/H_3PO_4	1:3		4320	350	60		1,157	(Yagmur et al., 2008)
Dates stones	Chemical/$ZnCl_2$	1:0.5			500	180		1,270	(Alhamed et al., 2009)
S.longifolium	Chemical/$ZnCl_2$	1:0.3			800	120	1,041	802	(Aravindhan et al., 2009)
H. valentiae	Chemical/$ZnCl_2$	1:0.3			800	120	962	783	(Aravindhan et al., 2009)
Olive-waste cakes,	Chemical/H_3PO_4	1:1.75	104	120	450	120	583	1,020	(Baccar et al., 2009)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Maize stalks	Chemical/KOH	1:1			700 (N_2)	60		1,684	(El-Hendawy, 2009)
Bean pods	Chemical/K_2CO_3	6:4	RT	720	950 (N_2)	10		1,580	(Cabal et al., 2009)
Cherry stones	Chemical/$ZnCl_2$	1:4	RT	1440	500	120		1,971	(Olivares-Marin et al., 2006)
Hemp fibers	Chemical/H_3PO_4	3:1			550	120		1,350	(Rosas et al., 2009)
Loquat stones	Chemical/KOH	1:2			1000	120		2,915	(Sutcu and Demiral, 2009)
Coffee husk	Chemical/$ZnCl_2$	1:1			550 (N_2)	180		900	(Oliveira et al., 2009)
Soybean oil cake	Chemical/K_2CO_3	1:1		1440	800	60		1,352	(Tay et al., 2009)

Table 2.5 Recent works on the production of activated carbon with physical activation.

Type of raw material	Type of activation	Condition				Activated carbon properties		reference
		Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
		Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Jatropha curcus	Physical/Steam			700	60	70	1	(Namasivayam et al., 2007)
P.oceanica leaf sheaths	Physical			600	60		111	(Ncibi et al., 2009)
Almond Shells	Physical/Steam	800	60	800	60		998	(Savova et al., 2001)
Grape seeds	Physical/Steam	800	60	800	60		497	(Savova et al., 2001)
Nut Shells	Physical/Steam	800	60	800	60		743	(Savova et al., 2001)
Pistachio-nut shell	Physical/CO_2	500	120	900	30		778	(Lua et al., 2004)

CHAPTER III

RESEARCH METHODOLOGY

3.1 Materials

3.1.1 Equipments

- Analytical Balance 4-digit (Adventurer, AR2140), Ohaus, USA
- Dessicator
- Muffle furnace: type ESF 12/23 (0-1200 °C), Carbolite, England.
- Spectrophotometer, Spectronic® UV/VIS Helios Alpha spectrophotometer with Vision32 software –v1.25
- Oven, (0-300 ^{o}C), WTC binder, Germany.
- Conical tube

3.1.2 Glassware

- Beakers
- Burette
- Pipettes
- Cylinders
- Erlenmeyer flasks
- Volumetric flasks
- Dropper

3.1.3 Chemical reagents

- Deionized water (DI water)
- Phosphoric acid (H_3PO_4), Scharlau
- Hydrochloric acid (HCl), Fisher chemical
- Iodine (I_2), Fisher scientific
- Starch solution, Asia pacific specialty chemical limited
- Potassium iodine (KI), Ajax Finechem
- Potassium iodate (KIO_3), Ajax Finechem
- Sodium thiosulfate ($Na_2SO_3.5H_2O$), CARLO ERBA
- Zinc chloride ($ZnCl_2$) , Ajax Finechem
- Potassium hydroxide (KOH), Ajax Finechem

3.2 Methods

3.2.1 Preparation of raw material

1. Wash the Jatropha seed cake, and shell with tap water
2. Dry the Jatropha seed cake, and shell in oven at 105°C for 240 minutes
3. Crush and sieve pass through mesh number 10 (2 mm)
4. Store in closed dessicator

3.2.2 Preparation of powder activated carbon at optimal temperature

1. Weigh 100 g of Jatropha seed cake, shell (from above) and impregnate into a 50 ml of phosphoric acid (85 wt%) (weight ratio of raw material and phosphoric acid is 1:0.5)
2. Stir thoroughly until well mixed at room temperature
3. Carbonize in a muffle furnace at 500°C
4. Wash the char with hot distilled water until the final pH reaches 6-8
5. Dry in oven at 105°C for 240 minutes
6. Crush and sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm)
7. Store powdered activated carbon in the dessicator
8. Repeat Steps 1-6 by changing activation temperature to 600 and 700°C

3.2.3 Preparation of powder activated carbon at optimal activation time

1. Weigh 100 g of Jatropha seed cake, shell and impregnate into a 50 ml of phosphoric acid (85 wt%) (weight ratio of raw material and phosphoric acid is 1:0.5)
2. Stir thoroughly until well mixed at room temperature
3. Carbonize the Jatropha seed cake, shell in a muffle furnace at suitable activation temperature (obtained from Section 3.2.2) for 60 minutes
4. Wash the activated carbon several times with hot distilled water until the pH value equals to 6
5. Dry at 105°C for 240 minutes

6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle

7. Repeat Steps 1-6 by changing activation time as 120 minutes and 180 minutes

3.2.4 Preparation of powder activated carbon at optimal weight ratio of raw material and phosphoric acid

1. Weigh 100 g of Jatropha seed cake, shell (from above) and impregnate into a 50 ml of phosphoric acid (85 wt%) (weight ratio of raw material and phosphoric acid is 1:0.5)

2. Stir thoroughly until well mixed at room temperature

3. Carbonize the Jatropha seed cake, shell in a muffle furnace at suitable activation temperature (obtained from Section 3.2.2) and activation time (as obtained from Section 3.2.3)

4. Wash the activated carbon with hot distilled water until the final pH reaches 6-8

5. Dry at 105^{o}C for 240 minutes

6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle

7. Repeat Steps 1-6 by changing impregnation ratio to 1:0.75 and 1:2

3.2.5 Preparation of powder activated carbon at optimal temperature

1. Weigh 100 g of Jatropha seed cake, shell (from above) and impregnate into a 50 ml of potassium hydroxide (55 wt%) (weight ratio of raw material and potassium hydroxide is 1:0.5)

2. Stir thoroughly until well mixed at room temperature

3. Carbonize in a muffle furnace at 500^{o}C

4. Wash the char with hot distilled water until the final pH reaches 6-8

5. Dry in oven at 105^{o}C for 240 minutes

6. Crush and sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm)

7. Store powdered activated carbon in the dessicator

8. Repeat Steps 1-6 by changing activation temperature to 600 and 700°C

3.2.6 Preparation of powder activated carbon at optimal activation time

1. Weigh 100 g of Jatropha seed cake, shell and impregnate into a 50 ml of potassium hydroxide (55 wt%) (weight ratio of raw material and potassium hydroxide is 1:0.5)

2. Stir thoroughly until well mixed at room temperature

3. Carbonize the Jatropha seed cake, shell in a muffle furnace at suitable activation temperature (obtained from Section 3.2.5) for 60 minutes

4. Wash the activated carbon several times with hot distilled water until the pH value equals to 6

5. Dry at 105°C for 240 minutes

6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle

7. Repeat Steps 1-6 by changing activation time as 120 minutes and 180 minutes

3.2.7 Preparation of powder activated carbon at optimal weight ratio of raw material and potassium hydroxide

1. Weigh 100 g of Jatropha seed cake, shell (from above) and impregnate into a 50 ml of potassium hydroxide (55 wt%) (weight ratio of raw material and potassium hydroxide is 1:0.5)

2. Stir thoroughly until well mixed at room temperature

3. Carbonize the Jatropha seed cake, shell in a muffle furnace at suitable activation temperature (obtained from Section 3.2.5) and activation time (as obtained from Section 3.2.6)

4. Wash the activated carbon with hot distilled water until the final pH reaches 6-8

5. Dry at 105°C for 240 minutes

6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle

7. Repeat Steps 1-6 by changing impregnation ratio to 1:0.75 and 1:2

3.2.8 Preparation of powder activated carbon at optimal temperature

1. Weigh 100 g of Jatropha seed cake, shell (from above) and impregnate into a 50 ml of zinc chloride (55 wt%) (weight ratio of raw material and zinc chloride is 1:0.5)
2. Stir thoroughly until well mixed at room temperature
3. Carbonize in a muffle furnace at 500^{o}C
4. Wash the char with hot distilled water until the final pH reaches 6-8
5. Dry in oven at 105^{o}C for 240 minutes
6. Crush and sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm)
7. Store powdered activated carbon in the dessicator
8. Repeat Steps 1-6 by changing activation temperature to 600 and 700^{o}C

3.2.9 Preparation of powder activated carbon at optimal activation time

1. Weigh 100 g of Jatropha seed cake, shell and impregnate into a 50 ml of zinc chloride (55 wt%) (weight ratio of raw material and zinc chloride is 1:0.5)
2. Stir thoroughly until well mixed at room temperature
3. Carbonize the Jatropha seed cake, shell in a muffle furnace at suitable activation temperature (obtained from Section 3.2.8) for 60 minutes
4. Wash the activated carbon several times with hot distilled water until the pH value equals to 6
5. Dry at 105^{o}C for 240 minutes
6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle
7. Repeat Steps 1-6 by changing activation time as 120 minutes and 180 minutes

3.2.10 Preparation of powder activated carbon at optimal weight ratio of raw material and zinc chloride

1. Weigh 100 g of Jatropha seed cake, shell (from above) and impregnate into a 50 ml of zinc chloride (55 wt%) (weight ratio of raw material and zinc chloride is 1:0.5)

2. Stir thoroughly until well mixed at room temperature

3. Carbonize the Jatropha seed cake, shell in a muffle furnace at suitable activation temperature (obtained from Section 3.2.8) and activation time (as obtained from Section 3.2.9)

4. Wash the activated carbon with hot distilled water until the final pH reaches 6-8

5. Dry at 105°C for 240 minutes

6. Sieve in the size ranged between mesh number 100 (0.150 mm) and 325 (0.045 mm) and store in closed bottle

7. Repeat Steps 1-6 by changing impregnation ratio to 1:0.75 and 1:2

3.2.11 Analysis of activated carbon properties

1. Iodine number is determined in the standard method ASTM 4607-94: see detail in Appendix A

2. Surface areas are calculated from the adsorption isotherms using the method of Brunauer, Emmet and Teller (BET). The BET surface area is determined by nitrogen adsorption (-196°C) on surface area analyzer (Thermo Finnigan, Sorptomatic 1990): see detail in Appendix B

3. The ash content of the carbon is determined using a standard method ASTM D 2866-94 (ASTM, 1996): see detail in Appendix C

4. Apparent (bulk) density of all samples is calculated as the ratio between weight and volume of packed dry material: see detail in Appendix D

5. Moisture content of activated carbon is determined according to the standard method ASTM D 2867-95: see detail in Appendix E

6. Chemical analysis of wood charcoal is examined according to the standard method ASTM D 1762-84: see detail in Appendix F

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

8. The yield of activated carbon is defined as the ratio of the weight of the final activated carbon to that of the initial weight Jatropha seed cake, stem, and shell with both weights on a dry basis, i.e.

$$\text{Yield} = \frac{W_1}{W_0} \text{x}\, 100 \tag{3-2}$$

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

9. The ultimate analysis of Jatropha seed cake, stem, shell is performed in CHNS/O analyzer (Perkin Elmer PE2400 Series II), using gaseous products freed by pyrolysis in high-purity oxygen and are chromatographically detected with a thermal conductivity detector. The proximate analysis is developed following ASTM standards for chemical analysis of wood charcoal (ASTM D 1762-84)

10. X-ray diffraction (XRD) patterns are obtained in a X-ray Diffraction Spectroscopy using Cu Kα radiation (λ=0.154056 nm), with a step size of 0.004° and a step time of 1.5 s

11. Fourier Transform Infrared Spectroscopy (FTIR) analysis. For this, the activated carbon samples are brought to constant weight in a drying oven at 50ºC for 24 hours and kept in the desiccators. Then 1 mg of dried granular activated carbon is mixed with 100 mg of KBr, which is initially dried at 110 ºC, in the sample disk. FTIR spectra in the range of 450-4000 cm^{-1} were obtained on a Perkin-Elmer, Model 1760X.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Properties of jatropha seed cake and shell

The properties of jatropha seed cake and shell were analyzed by several methods such as proximate analysis, ultimate analysis, bulk density and SEM etc. in order to compare the differences of raw materials. Table 4.1 displays results from the proximate analysis of jatropha seed cake and shell. The raw material suitable for the production of activated carbon should have a fixed carbon content of more than 30%. The carbon contents of jatropha seed cake and shell fell in this range and therefore they were considered suitable for the production of activated carbon. The ultimate analysis of jatropha seed cake and shell shown in Table 4.2 indicates that jatropha shell had higher carbon content than jatropha seed cake, on the other hand, it contained less hydrogen and nitrogen contents than the seed cake. Table 4.3 illustrates that jatropha seed cake had higher bulk density than jatropha shell.

4.2 Characteristics of activated carbon from jatropha seed cake and shell

100 grams of each seed cake and shell from Jatropha were washed with distilled water and dried at 100±10^{o}C. The dried material was milled, sieved and then mixed with chemical solutions (phosphoric acid, potassium hydroxide, and zinc chloride) at impregnation ratio of 1:0.5-1:2. The activated carbon was produced from those materials after pyrolyzed in furnace at activation temperature in range of 400-700^{o}C and activation time in range of 60-180 minutes. The efficiency of activated carbon was evaluated via iodine number. This number can be indicated their relative activation level and the surface area available for micropores. Usually adsorbents with high iodine number have a high surface area and suitable for adsorbing small compound. (Bestani et al., 2008) The detail of each activation agent is described as follows.

4.2.1 Activation with phosphoric acid

Table 4.4 displays the properties of the activation carbon from the seed cake. It illustrates that, at the impregnation ratio of 1:0.5 and preparation period of 60 minutes, iodine number increased with increasing temperature from 500-700^{o}C. Higher activation temperature reduced the volatile matter, which raised the fixed carbon content. However, too high temperature could impose adverse effect on the activated carbon property, e.g. iodine number was found to decrease at 800^{o}C possibly due to the destruction of porous structure and network at extremely high temperature. The optimal activation time was found at 120 minutes and 700^{o}C. A further increase in activation time resulted in a lower %yield because a long activation also promoted a more burn-off of carbonaceous matter and increased fixed carbon content. At 700^{o}C and 120 min, %yield decreased from 32 to 19 when the impregnation ratio increased from 1:0.5 to 1:1. This is because an excess amount of agent promoted the gasification of char, increasing the total weight loss of carbon. Bulk density of the activated carbon of jatropha seed cake and shell varied in the range of 0.48 – 0.57 g/cm^{3} and 0.43-0.53 g/cm^{3}, respectively (see Table 4.5). Increasing phosphoric acid content resulted in a more intense decomposition of the carbon surface, creating a larger pore, and this resulted in activated carbon with lower bulk density.

For the activated carbon from the shell, Table 4.5 illustrates that iodine number increased when temperature increased from 500-600^{o}C. Iodine number remained constant up to 700^{o}C because higher temperature led to a collapse of the pore structure and then enlarging pore size. At lower temperature and short activation time, the activation was only able to create low porosity char which led to a high %yield. An increase in activation time could lead to a depletion of surface, and a better removal of the volatile matter. This resulted in a reduction of %yield and a potential decrease in iodine number depending on the extent where the collapse of the pore occurred.

4.2.2 Activation with potassium hydroxide

Table 4.6 illustrates that, as activation temperature increased from 600-700^{o}C, the iodine number of the activated carbon derived from the jatropha seed cake increased from 354-609 mg/g. This was due to a better disengagement of chemical agent from the pore of the activated carbon at high temperature. In addition, increasing activation time extended the contact time between chemical agent and raw material resulted in development of pore structure and porous network, however, a longer activation time played an important role in lowering the yield as it caused more burn-off of the carbon creating a combination of micro-pores which led to a formation of meso-pore or macro-pore. Therefore the activation time should be long enough for the potassium hydroxide to contact the raw material in order to create sophisticating pore structure and high surface area but not too long to prevent the pore collapse. Increasing the impregnation ratio from 1:0.5 to 1:0.75 led to an increase in the iodine number from 636-696 mg/g. Bulk density of activated carbon for this case was around 0.3-0.4 g/cm^3. It should be noted from the results in Figure 4.4 that potassium hydroxide can better decompose the surface than phosphoric acid and zinc chloride, leading to a better formation of porous structure in the char.

The activation temperature with potassium hydroxide at 500 and 600^{o}C could not produce the activated carbon from jatropha shell. This might be possible as these temperatures were not enough to provide a completely reaction between the raw material and the chemical agent. Equations 2.3-2.5 in Section 2.6 indicated that the reaction between potassium hydroxide and carbon was only complete at around 650^{o}C. At 700^{o}C, extending the contact time from 60-120 minutes could enhance the iodine number to around 631-634 mg/g, but at the same time causing an excessive release of volatile matter which sacrificed the %yield from 21 to 12. This indicated that a too long contact time was not necessary as it did not improve the iodine number and further reduced the yield. An increase in the impregnation ratio from 1:0.5-1:0.75 decreased the iodine number from 634 to 576 mg/g because an increase in the chemical agent caused the promotion of the gasification of char, collapse of porous network leading to a formation of large size pore, which corresponded to a smaller surface area. In addition, ash content also increased due to the remaining potassium hydroxide in activated carbon.

4.2.3 Activation with zinc chloride

Table 4.8 illustrates that increasing the temperature enhanced the iodine number because high activation temperature supported the development of pore structure but decreased %yield. An increase in activation time decreased %yield of the activated carbon due to a greater release of volatile matter and moisture. A shorter activation time might not be enough for the release of volatile matter, and therefore it remained in the activated carbon leading to a higher %yield than that at a longer activation time. %yield of zinc chloride activation was the highest compared with the other chemical agents. This was because activated carbon from zinc chloride did not require intensive washing, resulting in a lesser loss of activated carbon. An increase in impregnation ratio from 1:0.5–1:0.75 increased iodine number from 446–525 mg/g because at high impregnation ratio, an excess chemical agent could penetrate deep into the structure of carbon generating tiny pore, but this reduced %yield from 64 – 51 due to a more intensified reaction that removed the carbon content and created high porosity structure. Bulk density of activated carbon with zinc chloride activation was the highest in the range of 0.77-1.23 g/cm^3 (jatropha seed cake) and 0.67-0.78 g/cm^3 (jatropha shell). It is noted that zinc is a heavy metal and when mixed with jatropha seed cake could increase the weight of the final activated carbon product.

Table 4.9 illustrates that an increase in activation temperature from 600-700^{o}C enhanced the iodine number from 303–343 mg/g. This is possible as increasing temperature allowed more volatile matter to be released than low activation temperature, and this is why %yield decreased from 40 to 38. An increase in activation time from 60 to 120 minutes increased the iodine number from 343 to 467 mg/g. This means that extending zinc chloride soaking time could intensify the attack of the zinc chloride on the jatropha shell structure. When the impregnation ratio increased from 1:0.5–1:0.75, iodine number decreased from 467–418 mg/g. This was because excess chemical agent decomposed the raw material more rigorously and therefore destroyed the porous network structure.

Previous works stated that the use of phosphoric acid as an activating agent could provide iodine number up to 1,096 mg/g. (Srinivasakannan et al., 2004) However, the result in this work showed maximum iodine number from the activation via potassium hydroxide at 696 mg/g. Although, this iodine number value is higher than that of standard of commercial activated carbon set by TIS 900-2532 at 600 mg/g, the activated carbon from jatropha seed cake and shell can only be classified in a moderate iodine number range. However, the application of activated carbon should be considered from other properties also as shown in the next sections.

4.3 Other properties of activated carbon products

4.3.1 Proximate properties

Tables 4.11 and 4.12 show the volatile matter, ash, and fixed carbon content of activated carbon from jatropha seed cake and shell, respectively, with various chemical agents, activation temperatures, activation times, and impregnation ratios. The ash content of activated carbon from jatropha seed cake and shell with phosphoric acid activation was the lowest resulting in an activated carbon product with higher fixed carbon content because the higher activation temperature reduces volatile matter content resulting in the decrease in %yield as observed in Section 4.2.

4.3.2 Ultimate properties

Table 4.13 illustrates that both activated carbon from jatropha seed cake and shell with phosphoric acid activation exhibited the highest carbon content because this activation method requires an extensive washing to neutralize the pH which resulted in a release of many other impurities. On the other hand, the carbon content of activated carbon with zinc chloride was the lowest, as the product obtained from this technique was with neutral pH and no extensive washing was required, and therefore there could be other non-carbon components remained on surface. This issue is further discussed in FTIR Section 4.6.

4.3.3 BET of activated carbon prepared at various conditions

Table 4.14 shows the surface area, average pore size, and total pore volume of activated carbon. The highest surface area of 699 m^2/g was obtained from the activated carbon from jatropha shell with potassium hydroxide activation with an impregnation ratio of 1:0.75 (raw material:chemical agent) at the activation temperature of 700^oC for 120 minutes which corresponded to the highest of iodine number reported in Section 4.2. The total pore volume was also the highest at 4.98 cm^3/g at this preparation condition. On the other hand, the average pore size of activated carbon from jatropha shell with zinc chloride was the largest, among all the conditions applied in this work at 9.86 nm. Pore structure is depicted by a SEM image which will be discussed in Section 4.4.

Table 4.10 illustrates that the maximum surface area in terms of BET number in this work was 699 mg g^{-1}. This was a relative moderate value compared to the other works. The different value of surface area can occurred from several reasons such as raw material, activation agent and activating conditions.

4.4 SEM

4.4.1 SEM images of activated carbon from jatropha seed cake and jatropha shell

The structure of the jatropha seed cake was smooth with no micropores (Figure 4.1). Figure 4.2 shows the SEM image of the jatropha shell where the micrographs show that the external surface was rougher than jatropha seed cake and no micropores were observed on the surface.

4.4.2 SEM images of activated carbon from jatropha seed cake with phosphoric acid activation

Figure 4.3 illustrates that, with an increase in the activation temperature from 600-700^{o}C, phosphoric acid could erode the material in order to create pore on the surface. This resulted in a larger pore area which answered why the iodine number for the activated carbon generated at this temperature range was high. Figure 4.3(b), (c) indicates that a longer activation time, e.g. 120 min, created a more regular pore when compared with the carbon prepared with a shorter activating period. At higher impregnation ratio, the phosphoric acid impregnation seems to develop larger sized pores than low impregnation ratio (Figure 4.3(c), (d)).

4.4.3 SEM images of activated carbon from jatropha seed cake with potassium hydroxide activation

Figure 4.4 is the surface morphology of the activated carbon after the activation process with potassium hydroxide. The activated carbon obtained at 700^{o}C had highly porous surface when compared to the activated carbon obtained at 600^{o}C (Fig 4.4(a), (b)). The effect of activation time at constant activation temperature and impregnation ratio is shown in Figure4.4(c), (d). The longer activation time developed more micropore and highly porous surface indicating relatively high surface area. A higher impregnation ratio resulted in the external surface of activated carbon being occupied with cavities, void and many small pores (Figure 4.4(c), (d)).

4.4.4 SEM images of activated carbon from jatropha seed cake with zinc chloride activation

Figure 4.5(a), (b) shows the differences of the external surfaces of the activated carbons prepared with zinc chloride at 600 and 700°C, respectively. At the activation temperature higher than 600°C, a highly microporous structure was generated at the outer surface. For the activation at 700°C, the longer activation time could lead to a formation of larger hole on surface (Fig 4.5(b), (d)). Comparison of the activated carbon morphology with increasing impregnation ratio from 1:0.5 to 1:0.75 as demonstrated in Fig 4.5(b), (c) illustrates that a higher impregnation ratio led to a more development of pores with different sizes on the carbon surface (Fig 4.5(c)). The activated carbon produced at this high impregnation ratio also exhibited high iodine number which meant that this condition provided the carbon with a large surface area and small pore size (Table 4.13).

4.4.5 SEM images of activated carbon from jatropha shell with phosphoric acid activation

Activation at 600°C with phosphoric acid resulted in the formation of many small pores of irregular size and shape on the external surface of activated carbon (Figure 4.6(a)). At 700°C of activation temperature and with the impregnation ratio of 1:0.5, the phosphoric acid seemed to be able to create more regular pore (Figure 4.6(c)). However, a much too long activation time could lead to a development of macropore due to the combination of micropore (Figure 4.6(b)).

4.4.6 SEM images of activated carbon from jatropha shell with potassium hydroxide activation

Figure 4.7(a), (b) is the comparison of the activated carbon at different activation times at a constant activation temperature (700°C) and impregnation ratio (1:0.5). A longer activation time led to a more development of porosity. This supports the notion that extended potassium hydroxide soaking time could intensify the attack the jatropha shell structure which resulted in a higher iodine number property (see Table 4.7). The impregnation ratio at 1:0.75 led to a formation of larger size pore, which corresponded to a smaller surface area. In addition, the washing and rinsing step might remove residual inorganic matter which could possibly block the pore entrance (Figure 4.7(b), (c)).

4.4.7 SEM images of activated carbon from jatropha shell with zinc chloride activation

Figure 4.8(a), (b) shows the activated carbon at different activation temperature. An increase in the activation temperature from 600 to 700^{o}C generated more pore on surface. The longer activation time (120 minutes) developed more micropore and highly porous surface indicating relatively high surface area as observed in Figure 4.8(c). A higher impregnation ratio facilitated the development of pore with regular size distribution, however, the developed pore seemed to be of larger size as seen in Figure 4.8(d) which corresponded well with average pore size as mention in Section 4.3.2.

4.5 X-ray Diffractometer

The structures of activated carbon were hexagonal graphite structure as indicated by XRD pattern at two broad peaks at 2θ of about 23^{o} and 43^{o}, respectively (Figure 4.9 (a)). Moreover, the XRD pattern of activated carbon shown in Figure4.9(b), (c) and (d) exhibited the broad peak at 2θ about 24^{o} which indicated that the activated carbon structure was amorphous. Figure 4.9(e) illustrates that activated carbon from jatropha shell with zinc chloride activation had amorphous structure with ZnO being found on surface which appeared as three sharp peaks at 2θ of about 32^{o} 34^{o} and 36^{o}, respectively. $Zn_5(OH)_8Cl_2{\cdot}H_2O$ was not found here which could be due to the fact that jatropha seed cake contained lesser quantity of water (moisture) when compared with jatropha shell. Figure 4.9 (f) illustrates that the activated carbon from jatropha shell with zinc chloride activation not only had amorphous structure with ZnO being found on the surface, but also contained the crystal of $Zn_5(OH)_8Cl_2{\cdot}H_2O$ (at 2θ of 11.2^{o} , 28.1^{o} ,33.5^{o}, and 37.9^{o}). This could be due to the reaction of zinc chloride and H_2O (moisture) in the raw material which formed $Zn_5(OH)_8Cl_2{\cdot}H_2O$. The

ZnO and $Zn_5(OH)_8Cl_2{\cdot}H_2O$ can be classified as impurities for this study because these crystals could possibly block the pore entrance. These two impurities could be eliminated by increase time in dehydration process.

4.6 FTIR

The existence of functional groups determines the acid-base character of activated carbons. The electrical charge of the surface groups may increase or decrease to adsorb target molecules. Generally, adsorbate has opposite electrostatic charge as the carbon surface or target molecule attracted with carbon surface resulting in increasing adsorption capacity. Table 4.15 summarizes the functional groups in seed cakes and activated carbon from seed cake whereas Table 4.16 illustrates those in jatropha shell and its derived activated carbon. These are described in detail below.

4.6.1 FTIR of jatropha seed cake and shell

Fig 4.10 shows the FTIR of jatropha seed cake. The broad band at 600 cm^{-1} was ascribed to the O-H band. The C-H out of plane bending in benzene derivative vibrations existed as apparent in the bands at 800 and 875 cm^{-1}. The band located at 1100 cm^{-1} corresponded to C-O vibration in alcohol. The band located at 1320, 1540, 1650 cm^{-1} were ascribed to C-O vibrations of carboxylate group, C=C vibrations of aromatic, and C=C of the olifinic, respectively. The sharp band located at 2850 and 2910 cm^{-1} corresponded to C-H vibration in methyl and methylene group. The strong broad band at 3400 cm^{-1} was ascribed to O-H stretching vibration in hydroxyl group involved in hydrogen bonds. The FTIR of jatropha shell is shown in Figure4.11. The broad band at 600 cm^{-1} was ascribed to the O-H band but at lower intensity than that of jatropha seed cake. The small band located at 800 and 900 cm^{-1} corresponded to the C-H out of plane bending in benzene derivative vibrations. The intensity of the broad band of hydroxyl groups located at 3400 cm^{-1} of jatropha shell was less than jatropha seed cake.

4.6.2 FTIR of activated carbon from jatropha seed cake with phosphoric acid activation

The absorption at 1190 cm^{-1} was tentatively assigned to the following phosphorous species: P-O, O–C stretching vibrations in P-O-C of aromatics and P-OOH. (Budinova et al., 2006) The band located at 1700 cm^{-1} was ascribed to phosphoric acid. This indicated that traces of phosphatic species remained in carbon matrix even after repeated washing. The band located at 750-890 cm^{-1} was ascribed to out-of-plane bending in benzene derivative vibrations which remained on surface after increasing activation temperature. (El-Hendawy. 2009; Girgis et al., 2009) The broad band located between 1080 cm^{-1} was attributable to C-O vibration. The band located at 500 cm^{-1} may be attributed to alphatic C-H species vibrations. A band appear in the spectra at 1590 cm^{-1} most likely was the C=C vibrations in aromatic rings after carbonization/activation. The strong band at 3400 cm^{-1} was ascribed to –OH streaching vibration in hydroxyl groups (El-Hendawy. 2009) (see Figure4.12, Table 4.15).

4.6.3 FTIR of activated carbon from jatropha seed cake with potassium hydroxide activation

In Figure 4.13, the strong band at 3400 cm^{-1} was ascribed to –OH stretching vibration in hydroxyl groups and mostly attributed to hydrogen bond participating in adsorbing water molecules. The hydroxyl groups maybe occurred from reaction of potassium hydroxide and raw material. The band located at 1600 cm^{-1} could be ascribed to olifinic C=C vibration. The band located between 1100 cm^{-1} and 1050 cm^{-1} were ascribed to C-O vibrations and R-OH groups in alcohol. The small band at 895 cm^{-1} was ascribed to C-H out of plane bending in benzene derivative vibration. The broad band at 600 cm^{-1} was ascribed to the O-H band (El-Hendawy. 2009) (See Table 4.15).

4.6.4 FTIR of activated carbon from jatropha seed cake with zinc chloride activation

Figure 4.14 illustrates that the small band at 870 cm^{-1} was ascribed to the C-H out of plane bending in benzene derivative vibration but this band disappeared after 120 minutes of activation at 700°C. The intense band at 1050 cm^{-1} could be assigned to alcohol R-OH group. The band located at 1600 cm^{-1} was ascribed to the presence of olefin C=C vibration. (Alhamed et al., 2009; El-Hendawy. 2009) The strong broad band located at 3420 cm^{-1} was ascribed to –OH stretching vibration in hydroxyl groups but this band disappeared when increasing activation time from 60 to 120 minutes (See Table 4.15).

4.6.5 FTIR of activated carbon from jatropha shell with phosphoric acid activation

Fig 4.15 illustrates that the band located at 950 cm^{-1} and 750 cm^{-1} may be attributed to aromatic group. At low activation temperature, i.e. 500-600^{o}C, the band located at 1220 cm^{-1} was ascribed to P=O, P-O-C aromatics, and P-OOH. The band located at 1700 cm^{-1} was ascribed to phosphoric acid. This indicated the remnants of phosphorus species in carbon matrix after repeated washing, however, this band disappeared when the activation temperature was raised up to 700^{o}C. This might be due to a tiny amount of phosphorus species at the surface which can be released at extreme temperature. The broad band located at 3400 cm^{-1} was ascribed to –OH stretching vibration in hydroxyl groups that also disappeared with the activation temperature of 700^{o}C. A band appear in the spectra at 1580 cm^{-1} most likely was the C=C vibrations in aromatic rings that also disappeared after carbonization/activation with activation temperature of 700^{o}C (See Table 4.16). Note that at temperature higher then 900^{o}C, phosphorus species left the carboneous surface completely and its FTIR peak was no longer observed. (Haimour, 2006)

4.6.6 FTIR of activated carbon from jatropha shell with potassium hydroxide activation

The broad band located between 1050 cm^{-1} and 1100 cm^{-1} was attributable to C-O vibration and R-OH groups in alcohol. The band located at 1510 – 1591 cm^{-1} corresponded to aromatic C=C group. Increasing impregnation ratio from 1:0.5 to 1:0.75 at the same activation temperature (700^{o}C) and activation time (120 minutes), caused the band at 600 cm^{-1}, 1100 cm^{-1}, and 1590 cm^{-1} to disappear which could be due to a requirement of repeated washing at high impregnation ratio (See Figure 4.16, Table 4.16).

4.6.7 FTIR of activated carbon from jatropha shell with zinc chloride activation

Figure 4.17 illustrates that the disappearing bands of C=C benzene ring and C-H stretching benzene ring located at 720 and 900 cm^{-1} were due to an increase in activation time, and these bands remained when impregnation ratio increased. The broad band located between 1050 cm^{-1} and 1100 cm^{-1} was attributable to C-O vibration and R-OH groups in alcohol that disappeared with both increases in activation time to 120 minutes and impregnation ratio to 1:0.75. The band located at 1600 cm^{-1} was ascribed to carboxylate group. This indicated that traces of carboxylate species remained in activated carbon despite increasing in both activation time (120 minutes) and impregnation ratio (1:0.75). The band around 3400 cm^{-1} corresponded to hydroxyl group and this disappeared with increasing activation time and impregnation ratio. The functional groups discovered on the surface of activated carbon with zinc chloride activation such as benzene ring, carboxylate species, and hydroxyl group derivative disappeared when the activation time was increased to 120 minutes (See Table 4.16).

4.7 Ultimate assessment of the effectiveness of activation techniques

The evaluation thus far only looked at the properties of the final activated carbons and did not consider the yield of the activated carbon which represents the quantity of the raw materials that could be converted to the useful product. The assessment in this section was designed to consider the yield and compare the properties of the activated carbon based on the initial weight of the raw material used in each case.

To be able to do this assessment, the following calculations have to be carried out:

Net iodine number:

$$\text{net iodine number} \quad = \quad \text{iodine number} \quad \times \quad \text{yield of activated carbon} \qquad (4\text{-}1)$$

$$\left(\frac{\text{mg iodine of activated carbon}}{\text{g of raw material}}\right) \left(\frac{\text{mg iodine of activated carbon}}{\text{g of activated carbon}}\right) \quad \left(\frac{\text{g of activated carbon}}{\text{g of raw material}}\right)$$

Net surface area:

$$\underset{\left(\frac{\text{m}^2\text{of activated carbon}}{\text{g of raw material}}\right)}{\text{net surface area}} = \underset{\left(\frac{\text{m}^2\text{of activated carbon}}{\text{g of activated carbon}}\right)}{\text{surface area}} \times \underset{\left(\frac{\text{g of activated carbon}}{\text{g of raw material}}\right)}{\text{yield of activated carbon}} \quad (4\text{-}2)$$

Tables 4.4 – 4.9 display the results of these calculations. For the jatropha seed cake, the highest net iodine number of 285 mg iodine/g of raw material seed cake was obtained from the activation with zinc chloride with an impregnation ratio of 1:0.5 (raw material:chemical agent) at the activation temperature of 700^{o}C for 120 minutes. It can be seen that, although the best activated carbon with the highest iodine number was obtained from the activation with potassium hydroxide, this method might not be the best as a large quantity of carbon was destroyed during the conversion process (only 16% survived with potassium hydroxide when compared with 64% in the case of zinc chloride). The activation with zinc chloride, despite of its lower effectiveness in creating high surface (for iodine adsorption), was considered better as the initial carbon could still be retained in the product and the total iodine adsorption was greater than those obtained from other methods.

For the activated carbon from jatropha shell, the highest net iodine number of 192 mg iodine/g of raw material (418 mg iodine/g of activated carbon) was obtained from the activation with zinc chloride with impregnation ratio of 1:0.75 (raw material: chemical agent) at the activation temperature of 700^{o}C for 60 minutes. This was, again, different from the conditions that gave the highest iodine number which was obtained from the activation with potassium hydroxide, where the iodine number was 634 mg iodine/g of activated carbon at activation temperature of 700^{o}C, 120 minutes, and impregnation ratio of 1:0.5. At this condition, the yield was only 12 g activated carbon/100 g raw material which rendered the net iodine number of only 76 mg iodine/g of raw material.

4.8 Economical aspect

The production cost of activated carbon constituted of several components, i.e. electricity cost, chemical agent cost, equipment cost, and deionize water for washing process. Table 4.15 shows the various expenses necessary for the production of activated carbon from jatropha seed cake (at the best condition presented in this work) with various chemical agents, i.e. phosphoric acid, potassium hydroxide and zinc chloride for 100 g of activated carbon, and these were approx. 123, 593 and 223 bahts, respectively. For jatropha activated carbon from shell, the costs at the best condition with various chemical agents, i.e. phosphoric acid, potassium hydroxide and zinc chloride for 100 g of activated carbon were approx. 323, 363 and 226 bahts, respectively (as shown in Table 4.16). It can be summarized that zinc chloride introduced the lowest cost of chemical agent compared with the others. Furthermore, zinc chloride exhibited the highest %yield and needed the lowest time for washing. On the other hand, activated carbons with phosphoric acid activation required a large amount of deionize water for washing process, consequently, increasing the production cost.

Incidentally, the production cost as revealed here was determined based on the laboratory scale production unit. For the industrial scale, a large amount of chemical agent and deionize water used to produce activated carbon could have come from the existing operation of the facility and this might provide a cheaper cost per unit of production.

4.9 Applications

Applications of activated carbon can be adapted from its properties such as pore size, functional group on surface. The activated carbon with zinc chloride suited for removal of cationic dye from aqueous solution. (Malik et al., 2007) The non-polar activated carbon can be excellent for the adsorption of organic substances such as, mineral oil, poly aromatic hydrocarbons, chloride, and phenol. The activated carbon containing high concentration of O-H hydrogen bond is used to adsorb water. Adsorption of metal such as mercury, cadmium, lead requires high concentration of oxygen-containing functional groups such as carboxylic, phenol, lactone group etc. on the surface of activated carbon. A summary of the potential applications for the activated carbons generated from this work is given in Table 4.19.

Table 4.1 Proximate analysis of Jatropha seed cake and shell (dry basis)

Sample	Volatile (%)	Ash (%)	Fixed carbon (%)
Seed cake	59.16	6.99	33.85
Shell	43.03	16.25	40.72

Table 4.2 Ultimate analysis of Jatropha seed cake and shell

Sample	C (%)	H (%)	N (%)	S (%)	Other (%)
Seed cake	37.2	4.36	0.23	0.67	57.54
Shell	44.2	6.27	5.66	0.81	43.06

Table 4.3 Bulk density of Jatropha seed cake and shell

Sample	Bulk density (g/cm^3)
Seed cake	0.73
Shell	0.41

Table 4.4 Properties of activated carbon from jatropha seed cake with phosphoric acid activation

Impregnation Ratio (Cake:H_3PO_4)	Condition		%yield	Iodine number (mg/g)	Net iodine number (mg/g)	Bulk density (g/cm^3)
	Temp. (^{o}C)	Time (min.)				
1:0.5	500	60	50	201	100	0.77
1:0.5	600	60	36	360	130	0.52
1:0.5	700	60	33	423	140	0.49
1:0.5	800	60	31	344	107	0.48
1:0.5	700	60	33	423	140	0.49
1:0.5	700	120	32	516	165	0.54
1:0.5	700	180	30	347	104	0.57
1:1	700	120	19	409	78	0.44

Table 4.5 Properties of activated carbon from jatropha shell with phosphoric acid activation

Impregnation Ratio (Shell:H_3PO_4)	Condition		%yield	Iodine number (mg/g)	Net iodine number (mg/g)	Bulk density (g/cm^3)
	Temp. (^{o}C)	Time (min.)				
1:0.5	500	60	28	337	270	0.45
1:0.5	600	60	40	461	184	0.40
1:0.5	600	120	38	420	160	0.53
1:0.5	700	60	26	460	120	0.54

Table 4.6 Properties of activated carbon from jatropha seed cake with potassium hydroxide activation

Impregnation Ratio (Cake:KOH)	Condition		%yield	Iodine number (mg/g)	Net iodine number (mg/g)	Bulk density (g/cm^3)
	Temp. (^{o}C)	Time (min.)				
1:0.5	600	60	25	354	89	0.36
1:0.5	700	60	20	558	112	0.43
1:0.5	700	120	22	609	134	0.44
1:0.5	700	180	21	636	134	0.42
1:0.75	700	180	16	696	111	0.32

Table 4.7 Properties of activated carbon from jatropha shell with potassium hydroxide activation

Impregnation Ratio (Shell:KOH)	Condition		%yield	Iodine number (mg/g)	Net iodine number (mg/g)	Bulk density (g/cm^3)
	Temp. (^{o}C)	Time (min.)				
1:0.5	700	60	21	631	133	0.45
1:0.5	700	120	12	634	76	0.37
1:0.75	700	60	11	576	63	0.29

Table 4.8 Properties of activated carbon from jatropha seed cake with zinc chloride activation

Impregnation Ratio (Cake:$ZnCl_2$)	Condition		%yield	Iodine number (mg/g)	Net iodine number (mg)	Bulk density (g/cm^3)
	Temp. (^oC)	Time (min.)				
1:0.5	500	60	44	95	43	0.84
1:0.5	600	60	50	82	41	0.77
1:0.5	700	60	53	413	219	0.83
1:0.5	700	120	64	446	285	1.23
1:0.5	700	180	45	350	158	1.11
1:0.75	700	120	51	525	268	1.00
1:1	700	120	44	495	218	0.95

Table 4.9 Properties of activated carbon from jatropha shell with zinc chloride activation

Impregnation Ratio (Shell:$ZnCl_2$)	Condition		%yield	Iodine number (mg/g)	Net iodine number (mg)	Bulk density (g/cm^3)
	Temp. (^oC)	Time (min.)				
1:0.5	600	60	40	303	121	0.74
1:0.5	700	60	38	343	130	0.70
1:0.5	700	120	41	467	191	0.67
1:0.75	700	60	46	418	192	0.78

Table 4.10 Comparison for the properties of the iodine number from this work with the other recent works

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
Hazelnut shell	Chemical/$ZnCl_2$				800	120	965	793	(Aygun et al., 2003)
Rubber wood sawdust	Chemical/H_3PO_4	1:1.5			500	45	1,096	1,496	(Srinivasakannan et al., 2004)
Rosa canina fruits	Chemical/$ZnCl_2$	1:5			500	60	495	800	(Gurses et al., 2006)
Date stone wastes	Chemical/H_3PO_4	1:0.4	RT	1440	800	60	495		(Haimour and Emeish, 2006)
Eucalyptus dehn bark	Chemical/H_3PO_4	1:1			500	60	1,043	1,239	(Patnukao and Pavasant, 2008)
Activated sludge	Chemical/KOH	1:2.5	RT	1440	600	60	563	382	(Wang et al., 2008)

Type of raw material	Condition						Activated carbon properties		reference
	Type of activation	Ratio	Carbonization		Activation		Iodine number (mg/g)	Surface area (m^2/g)	
			Temperature (°C)	Time (min.)	Temperature (°C)	Time (min.)			
S.longifolium	Chemical/$ZnCl_2$	1:0.3			800	120	1,041	802	(Aravindhan et al., 2009)
H. valentiae	Chemical/$ZnCl_2$	1:0.3			800	120	962	783	(Aravindhan et al., 2009)
Olive-waste cakes	Chemical/H_3PO_4	1:1.75	104	120	450	120	583	1,020	(Baccar et al., 2009)
Jatropha seed cake	Chemical/H_3PO_4	1:0.5			700	120	516	507	This work
	Chemical/KOH	1:0.75			700	180	696	666	
	Chemical/$ZnCl_2$	1:0.75			700	120	525	567	
Jatropha shell	Chemical/H_3PO_4	1:0.5			600	60	461		This work
	Chemical/KOH	1:0.5			700	120	634	699	
	Chemical/$ZnCl_2$	1:0.5			700	60	467		

Table 4.11 Proximate analysis of activated carbon from jatropha seed cake

No.	Condition*	Volatile matter (%)	Ash (%)	Fixed carbon (%)
1	H_3PO_4 500^oC (60 min) 1:0.5	32.55	4.06	63.40
2	H_3PO_4 600^oC (60 min) 1:0.5	18.76	3.73	77.50
3	H_3PO_4 700^oC (60 min) 1:0.5	14.28	4.23	81.49
4	H_3PO_4 700^oC (120 min) 1:0.5	15.17	4.93	79.90
5	H_3PO_4 700^oC (120 min) 1:1	13.24	9.63	77.12
6	KOH 600^oC (60 min) 1:0.5	22.06	22.58	55.35
7	KOH 700^oC (60 min) 1:0.5	16.82	21.54	61.64
8	KOH 700^oC (120 min) 1:0.5	1.04	13.79	85.17
9	KOH 700^oC (120 min) 1:0.75	26.94	17.09	55.97
10	$ZnCl_2$ 500^oC (60 min) 1:0.5	32.69	22.50	44.80
11	$ZnCl_2$ 600^oC (60 min) 1:0.5	27.71	23.12	49.17
12	$ZnCl_2$ 700^oC (60 min) 1:0.5	11.36	27.67	60.97
13	$ZnCl_2$ 700^oC (120 min) 1:0.5	13.58	27.36	59.06
14	$ZnCl_2$ 700^oC (180 min) 1:0.5	18.95	18.82	62.23
15	$ZnCl_2$ 700^oC (120 min) 1:0.75	11.87	23.74	64.39
16	$ZnCl_2$ 700^oC (120 min) 1:1	14.96	22.28	62.76

* This column reports the following items in this exact order: Activating agent, activation temperature (reaction time), impregnation ratio between raw material: chemical agent.

Table 4.12 Proximate analysis of activated carbon from jatropha shell

No.	Condition*	Volatile matter (%)	Ash (%)	Fixed carbon (%)
1	H_3PO_4 600^{o}C (60 min) 1:0.5	19.16	7.02	73.83
2	H_3PO_4 600^{o}C (120 min) 1:0.5	11.07	4.69	84.25
3	H_3PO_4 700^{o}C (60 min) 1:0.5	18.35	4.46	77.19
4	KOH 700^{o}C (60 min) 1:0.5	27.25	38.40	34.35
5	KOH 700^{o}C (120 min) 1:0.5	13.81	35.62	50.57
6	KOH 700^{o}C (60 min) 1:0.75	14.29	36.58	49.13
7	$ZnCl_2$ 600^{o}C (60 min) 1:0.5	32.70	40.32	26.98
8	$ZnCl_2$ 700^{o}C (60 min) 1:0.5	28.52	37.27	34.21
9	$ZnCl_2$ 700^{o}C (120 min) 1:0.5	13.03	33.11	53.87
10	$ZnCl_2$ 700^{o}C (60 min) 1:0.75	13.14	35.68	51.18

* This column reports the following items in this exact order: Activating agent, activation temperature (reaction time), impregnation ratio between raw material: chemical agent.

Table 4.13 Ultimate analysis of activated carbon

Raw material	Condition*	C (%)	H (%)	N (%)	Other (%)
Seed cake	H_3PO_4 700°C(120 min) 1:0.5	66.52	2.27	1.78	29.43
Seed cake	KOH 700°C (180 min) 1:0.75	63.98	1.87	0.73	33.42
Seed cake	$ZnCl_2$ 700°C (120 min) 1:0.75	63.75	2.07	2.23	31.95
Shell	H_3PO_4 600°C (60 min) 1:0.5	73.62	2.56	1.53	22.29
Shell	KOH 700°C (120 min) 1:0.5	59.70	2.14	0.48	37.68
Shell	$ZnCl_2$ 700°C (60 min) 1:0.5	41.32	1.69	1.09	55.90

* This column reports the following items in this exact order: activating agent, activation temperature (reaction time), impregnation ratio between raw material: chemical agent.

Table 4.14 BET of activated carbon

Raw material	Condition*	Surface area (m^2/g)	Average pore size (nm)	Net surface area (m^2/g)	Total pore volume (cm^3/g)
Seed cake	H_3PO_4 700°C (120 min.) 1:0.5	507	4.97	162	0.63
Seed cake	KOH 700°C (180 min.) 1:0.75	666	2.37	107	0.39
Seed cake	$ZnCl_2$ 700°C (120 min.) 1:0.75	567	2.19	289	0.33
Shell	KOH 700°C (120 min.) 1:0.5	699	2.85	84	4.98
Shell	$ZnCl_2$ 700°C (60 min.) 1:0.5	65	9.86	25	1.61

* This column reports the following items in this exact order: Activating agent, activation temperature (reaction time), impregnation ratio between raw material: chemical agent.

Table 4.15 FTIR of activated carbon from jatropha seed cake

Assignment	Frequency (cm^{-1})								
	Before	After							
		Z	P,K,Z	P,K,Z	P,K,Z	K	K,Z	P	K
		500°C (60) 1:0.5	600°C (60) 1:0.5	700°C (60) 1:0.5	700°C (120) 1:0.5	700°C (180) 1:0.5	700°C (120) 1:0.75	700°C (120) 1:1	700°C (180) 1:0.75
Phosphoric species									
P-O, P-O-C, P-OOH (out of plane)	-	-	P	P	P	-	-	P	-
P-O (stretching)	-	-	P	-	P	-	-	-	-
Alcohols									
O-H (out of plane)	√	Z	K,Z	K,Z	Z	-	Z	-	-
C-O (stretching)	√	-	P,K	P,K	P	-	-	P	-
Olifinic group									
C=C (stretching)	√	Z	P,K,Z	P,K,Z	P,Z	-	-	P	-

Alphatic derivative									
C-H (Stretching)	-	-	P	-	P	-	-	-	-
Benzene derivative									
C-H (Out of plane)	√	Z	P,K,Z	P,K	P	-	-	-	-
Aromatic rings									
C=C (Stretching)	√	-	P	P	P	-	-	P	-
Carboxylate group									
C-O (stretching)	√	-	-	-	-	-	-	-	-
Methyl group									
C-H (stretching)	√	-	-	-	-	-	-	-	-
Hydroxyl group									
O-H (stretching)	√	Z	P,K,Z	P,K,Z	P	-	-	P	-

Remarks: P = phosphoric acid activation, K = potassium hydroxide activation, Z = zinc chloride activation

Table 4.16 FTIR of activated carbon from jatropha shell

Assignment	Frequency (cm^{-1})						
	Before	After					
		P	P,Z	P,K,Z	K,Z	K	Z
		500^{o}C (60) 1:0.5	600^{o}C (60) 1:0.5	700^{o}C (60) 1:0.5	700^{o}C (120) 1:0.5	700^{o}C (120) 1:0.75	700^{o}C (60) 1:0.75
Phosphoric species							
P-O, P-O-C, P-OOH (out of plane)	-	P	P	-	-	-	-
P-O (stretching)	-	P	P	-	-	-	-
Olifinic group							
C=C (stretching)	-	-	Z	Z	Z	-	Z
Benzene derivative							
C-H (Out of plane)	√	P	P,Z	Z	Z	-	Z
C=C (stretching)	-	-	Z	Z	Z	-	Z

Alcohols							
O-H (out of plane)	√	-	-	-	-	-	-
R-OH (stretching)	√	-	Z	Z	Z	-	Z
C-O (stretching)	-	-	-	K	K	-	-
Aromatic rings							
C=C (Stretching)	-	P	P	K	K	-	-
Carboxylate group							
C-O (stretching)	√	-	-	-	-	-	-
Methyl group							
C-H (stretching)	√	-	-	-	-	-	-
Hydroxyl group							
O-H (stretching)	√	P	P,Z	Z	-	-	-

Remarks: P = phosphoric acid activation, K = potassium hydroxide activation, Z = zinc chloride activation

Table 4.17 Production cost of activated carbon from jatropha seed cake

Information	Phosphoric acid[1] (85%w/w)	Potassium hydroxide[2] (55% w/w)	Zinc chloride[3] (55% w/w)
Chemical agent requirement			
- Chemical agent charge	500 THB/L	450 THB/kg	1540 THB/kg
- Amount of chemical agent	0.05 L	0.04 kg	0.04 kg
Total chemical agent charge	25 THB	18.5 THB	63.6 THB
Electricity requirement			
- Furnace	6.2 kWh	9.3 kWh	6.2 kWh
- Oven	6.4 kWh	6.4 kWh	6.4 kWh
Total electricity requirement	12.6 kWh	15.7 kWh	12.6 kWh
Electricity charge	2 THB/kWh	2 THB/kWh	2 THB/kWh
Total electricity charge	25.2 THB	31.4 THB	25.2 THB
Water requirements			
- DI water	20 L	10 L	5 L
Water charge	4000 THB/m^3	4000 THB/m^3	4000 THB/m^3
Total water charge	80 THB	40 THB	20 THB
Equipment requirements			
- Earthenware	5 THB	5 THB	5 THB
Total equipment charge	5 THB	5 THB	5 THB
%yield	32 %	16 %	51%
[4] Total expenses	423 THB	593 THB	223 THB

[1] Condition: 700°C, 120 minutes, and 1:0.5 (temperature, time, and impregnation ratio)

[2] Condition: 700°C, 180 minutes, and 1:0.75 (temperature, time, and impregnation ratio)

[3] Condition: 700°C, 120 minutes, and 1:0.75 (temperature, time, and impregnation ratio)

[4] Basis: 100 grams of activated carbon

Table 4.18 Production cost of activated carbon from jatropha shell

Information	Phosphoric acid[1] (85%w/w)	Potassium hydroxide[2] (55% w/w)	Zinc chloride[3] (55% w/w)
<u>Chemical agent requirement</u>			
- Chemical agent charge	500 THB/L	450 THB/kg	1540 THB/kg
- Amount of chemical agent	0.05 L	0.03 kg	0.03 kg
Total chemical agent charge	25 THB	12.4 THB	43.4 THB
<u>Electricity requirement</u>			
- Furnace	3.1 kWh	3.1 kWh	6.2 kWh
- Oven	6.4 kWh	6.4 kWh	6.4 kWh
Total electricity requirement	9.5 kWh	9.5 kWh	12.6 kWh
Electricity charge	2 THB/kWh	2 THB/kWh	2 THB/kWh
Total electricity charge	19 THB	19 THB	25.2 THB
<u>Water requirements</u>			
- DI water	20 L	10 L	5 L
Water charge	4000 THB/m^3	4000 THB/m^3	4000 THB/m^3
Total water charge	80 THB	40 THB	20 THB
<u>Equipment requirements</u>			
- Earthenware	5 THB	5 THB	5 THB
Total equipment charge	5 THB	5 THB	5 THB
%yield	40 %	21 %	41%
[4]Total expenses	323 THB	363 THB	226 THB

[1] Condition: 600°C, 60 minutes, and 1:0.5 (temperature, time, and impregnation ratio)

[2] Condition: 700°C, 60 minutes, and 1:0.5 (temperature, time, and impregnation ratio)

[3] Condition: 700°C, 120 minutes, and 1:0.5 (temperature, time, and impregnation ratio)

[4] Basis: 100 grams of activated carbon

Table 4.19 Application of activated carbon from this work

Raw material	Chemical agent	Activation condition*	Properties	Application
Jatropha seed cake	Phosphoric acid	700^{o}C, 120 minutes, and 1:0.5	- Hydroxyl group on surface	- Adsorption of water such as azeotrope system
	Potassium hydroxide	700^{o}C, 180 minutes, and 1:0.75	- No functional groups - High surface area - Small average pore size	- Adsorption of small organic substances
	Zinc chloride	700^{o}C, 120 minutes, and 1:0.75	- No functional groups	- Adsorption of organic substances
Jatropha shell	Phosphoric acid	600^{o}C, 60 minutes, and 1:0.5	- No functional groups	- Adsorption of organic substances
	Potassium hydroxide	700^{o}C, 60 minutes, and 1:0.5	- No functional groups - Small average pore size - microporosity material	- Adsorption of small organic substances
	Zinc chloride	700^{o}C, 120 minutes, and 1:0.5	- Carboxylate group on surface	- Adsorption of metal ions

*This column reports the following items in this exact order: Activation temperature, reaction time, and impregnation ratio between raw material: chemical agent.

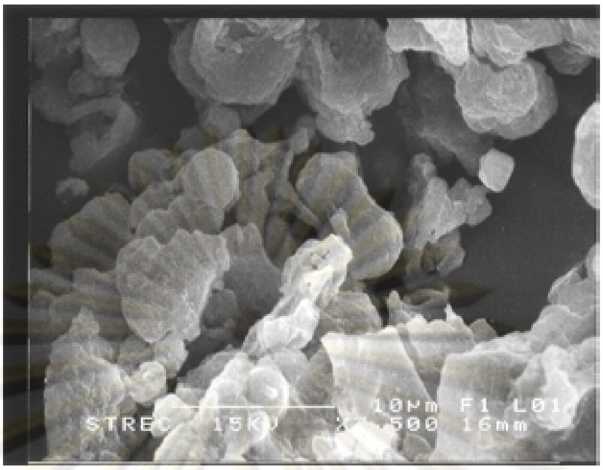

Figure 4.1 SEM image of jatropha seed cake

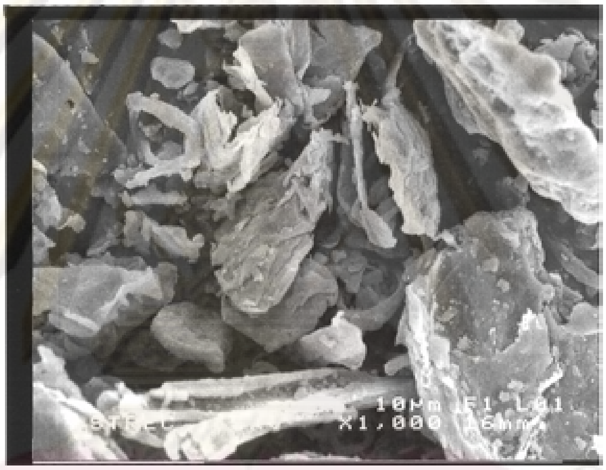

Figure 4.2 SEM image of jatropha shell

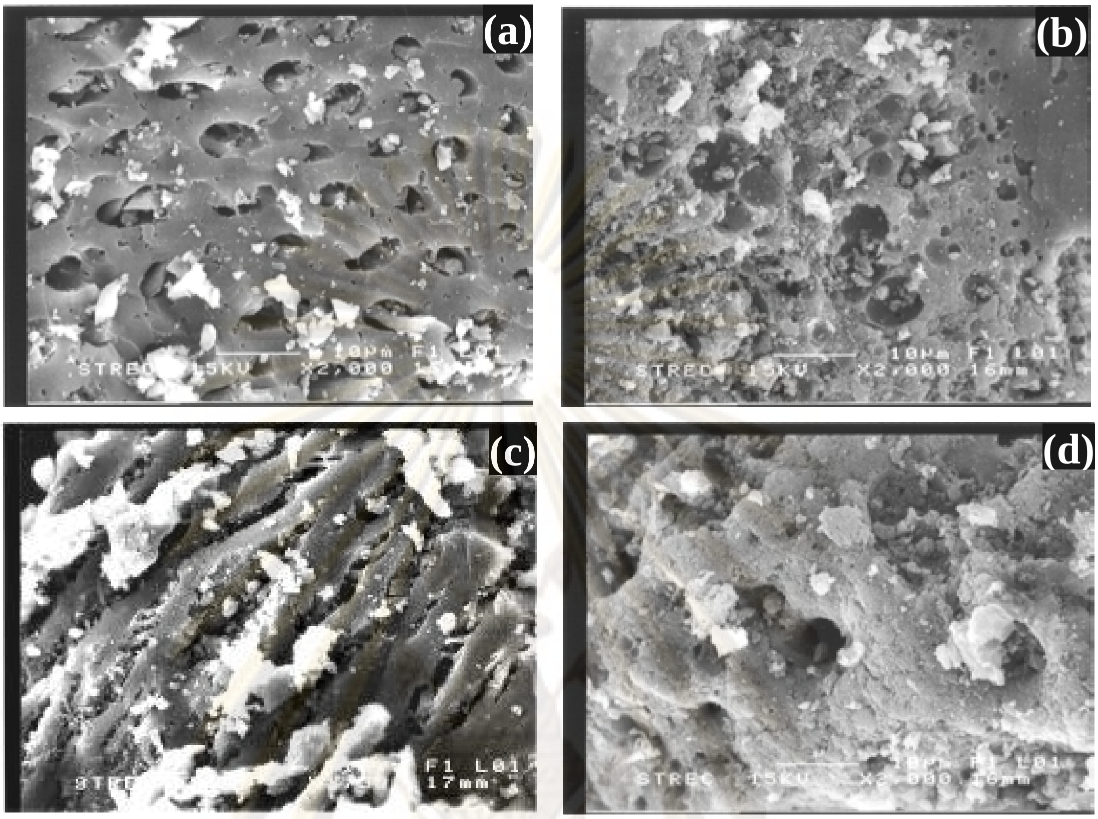

Figure 4.3 SEM images of activated carbon from jatropha seed cake with phosphoric acid activation at activation temperature, activating time, and impregnation ratio of: (a) 600^{o}C 60 min, and 1:0.5; (b) 700^{o}C 60 min, and 1:0.5; (c) 700^{o}C 120 min, and 1:0.5; (d) 700^{o}C 120 min, and 1:1

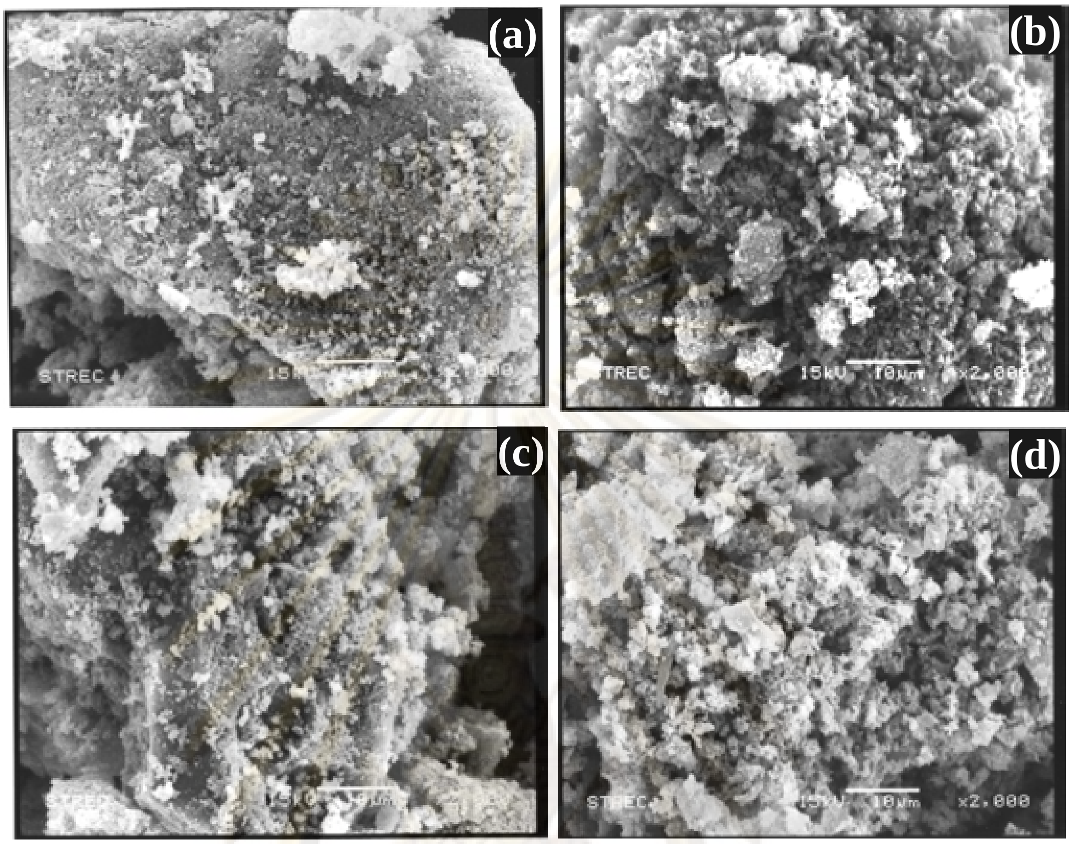

Figure 4.4 SEM images of activated carbon from jatropha seed cake with potassium hydroxide activation at activation temperature, activating time, and impregnation ratio of**:** (a) 600^{o}C 60 min, and 1:0.5 (b) 700^{o}C 60 min, and 1:0.5(c) 700^{o}C 120 min, and 1:0.5 (d) 700^{o}C 180 min, and 1:0.75

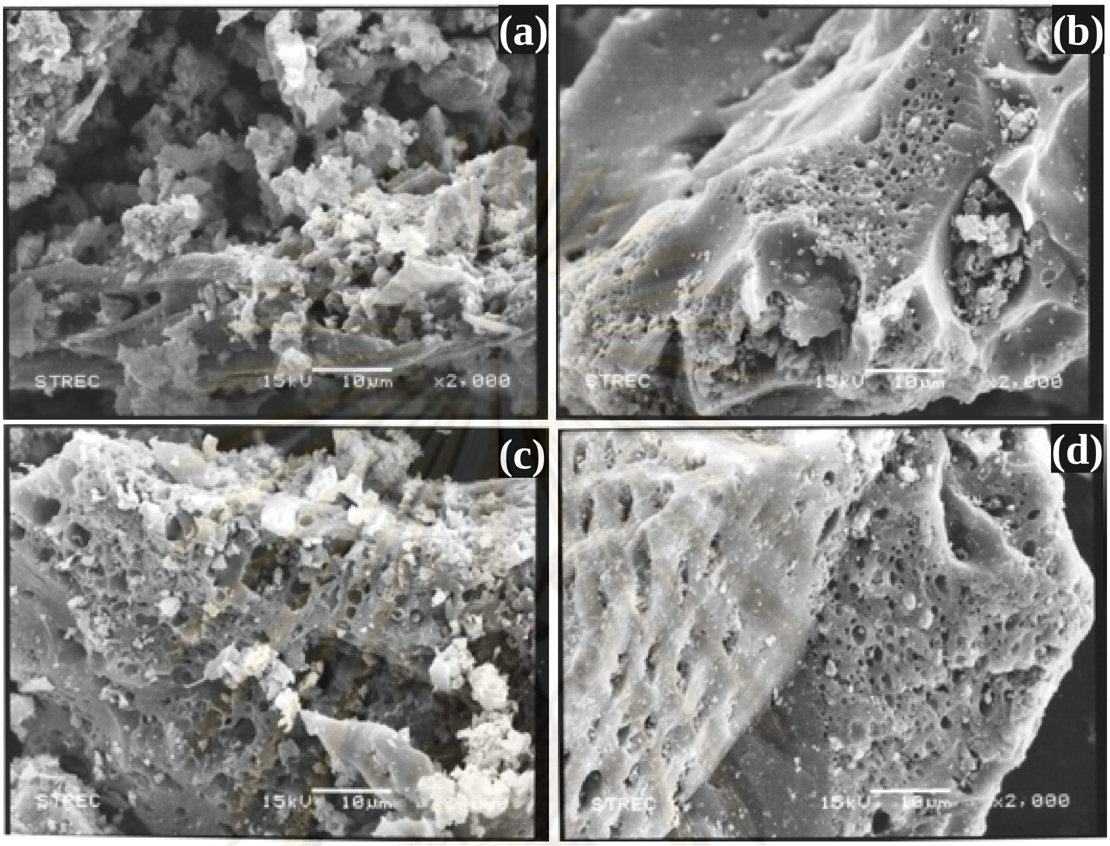

Figure 4.5 SEM images of activated carbon from jatropha seed cake with zinc chloride activation at activation temperature, activating time, and impregnation ratio of: (a) 600^{o}C 60 min, and1:0.5 (b) 700^{o}C 60 min, and 1:0.5 (c) 700^{o}C 120 min, and 1:0.75 (d) 700^{o}C 180 min, and 1:0.5

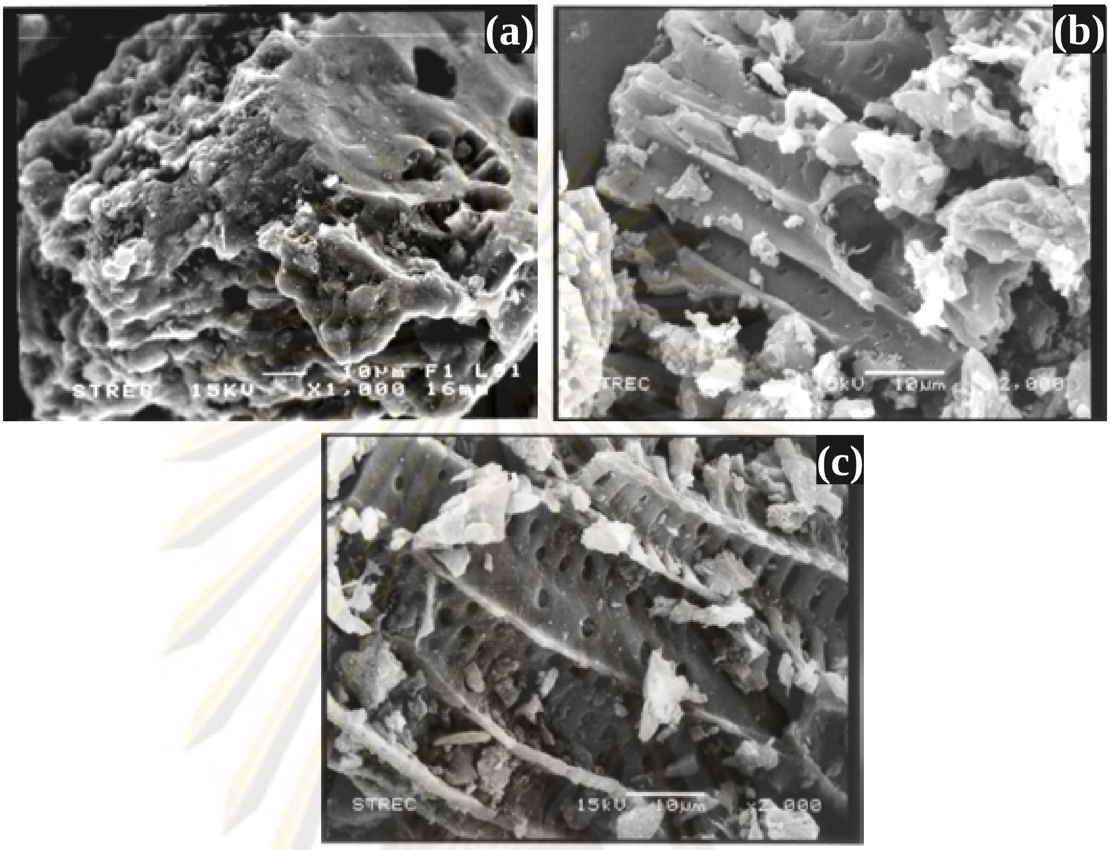

Figure 4.6 SEM images of activated carbon from jatropha shell with phosphoric acid activation at activation temperature, activating time, and impregnation ratio of: (a) 600^{o}C 60 min, and 1:0.5 (b) 600^{o}C 120 min, and1:0.5 (c) 700^{o}C 60 min, and1:0.5

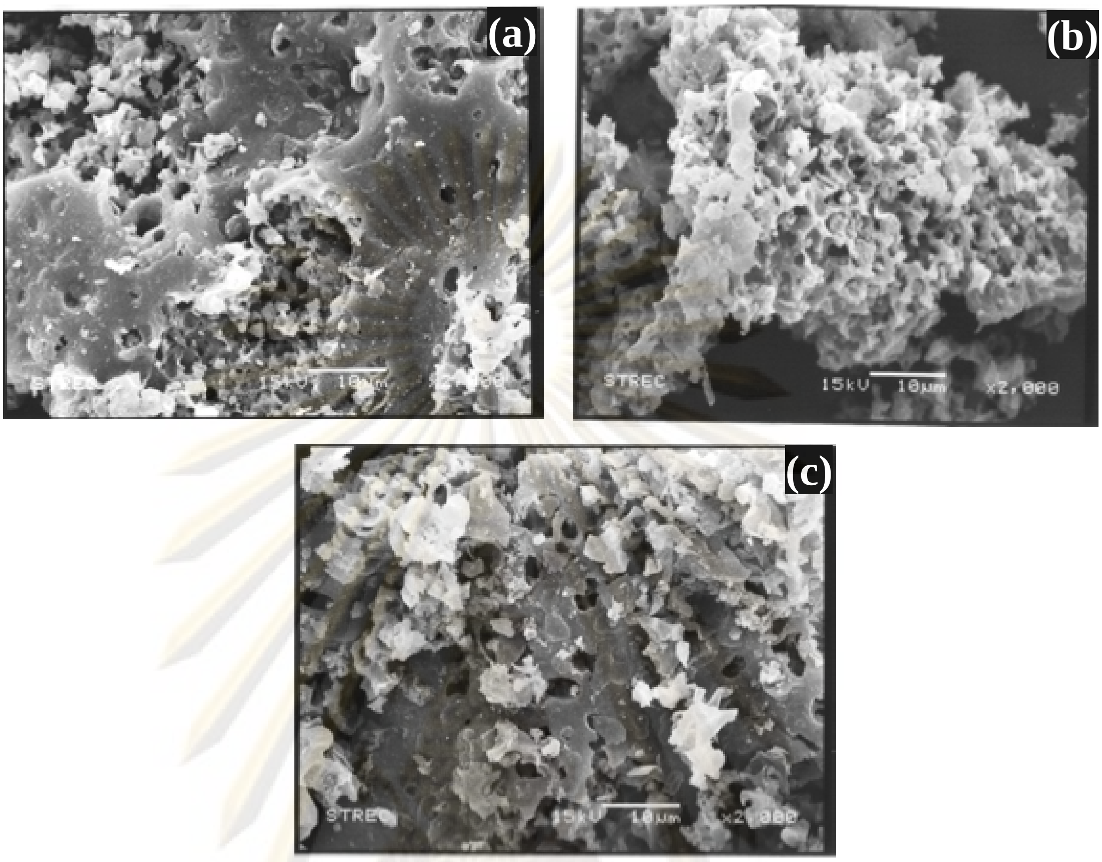

Figure 4.7 SEM image of activated carbon from jatropha shell with potassium hydroxide activation at activation temperature, activating time, and impregnation ratio of: (a) Condition: 700^{o}C 60 minutes 1:0.5 (b) Condition: 700^{o}C 120 minutes 1:0.5 (c) Condition: 700^{o}C 60 minutes 1:0.75

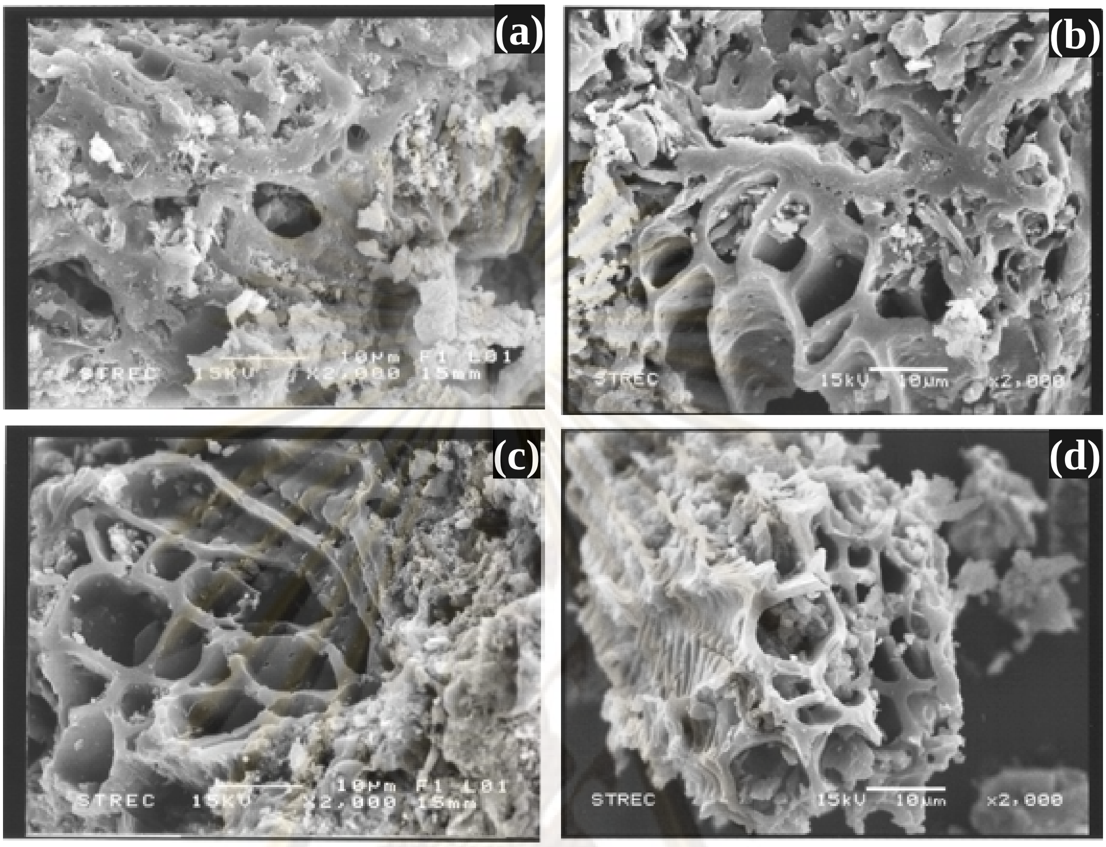

Figure 4.8 SEM image of activated carbon from jatropha shell with zinc chloride activation at activation temperature, activating time, and impregnation ratio of: (a) Condition: 600^{o}C 60 minutes 1:0.5 (b) Condition: 700^{o}C 60 minutes 1:0.5 (c) Condition: 700^{o}C 120 minutes. 1:0.5 (d) Condition: 700^{o}C 60 minutes 1:0.75

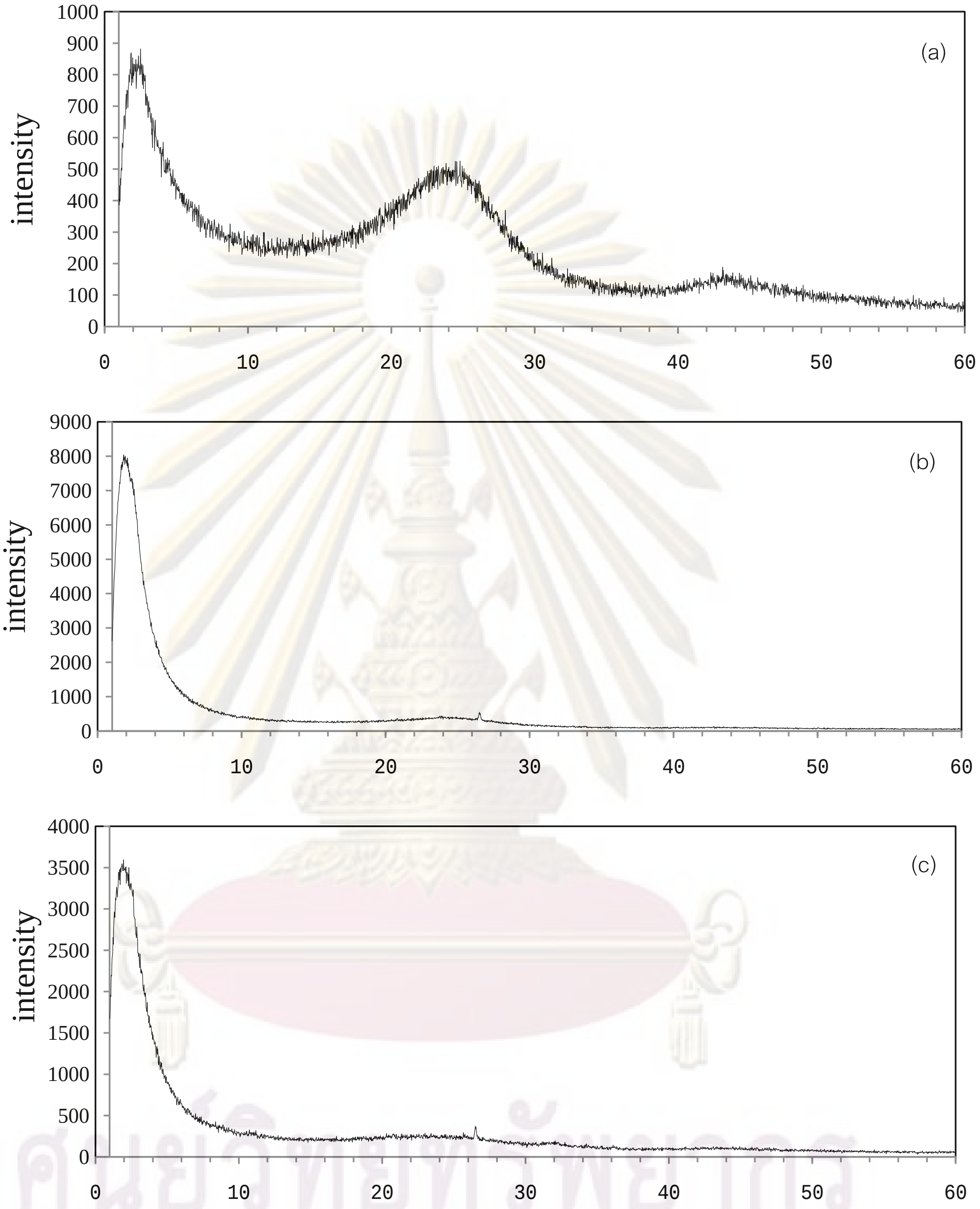

Figure 4.9 XRD of the activated carbon from: (Raw material: Activating chemical: Activation temperature: Activation time: Ratio between raw material: chemical agent)

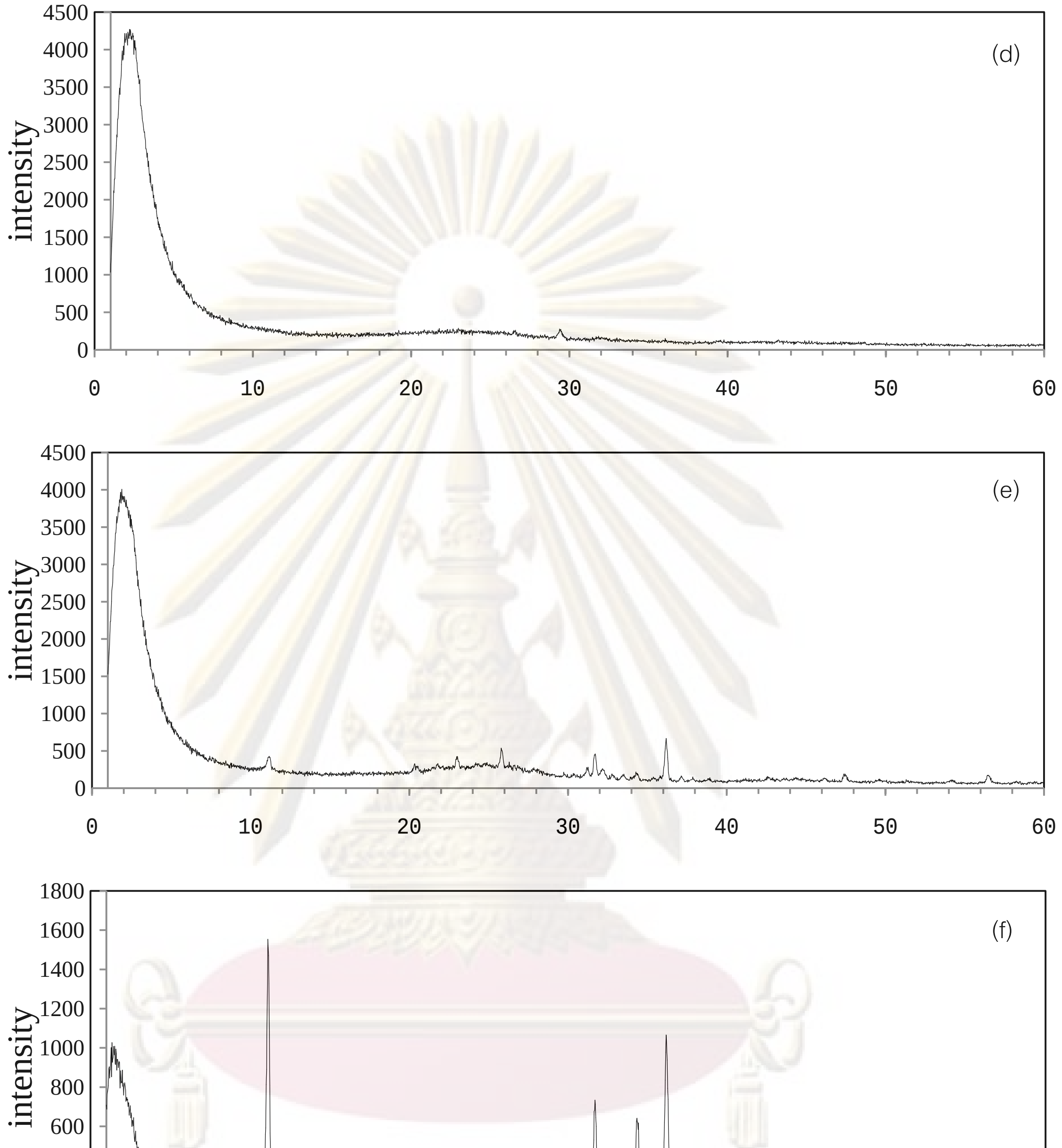

Figure 4.9 (cont.) XRD of the activated carbon from: (Raw material: Activating chemical: Activation temperature: Activation time: Ratio between raw material: chemical agent)

(a) Seed cake: H_3PO_4: 700^oC: 120 min: 1:0.5 (b) Shell: H_3PO_4: 600^oC: 60 min: 1:0.5

(c) Seed cake: KOH: 700^oC: 180 min: 1:0.75 (d) Shell: KOH: 700^oC: 120 min: 1:0.5

(e) Seed cake: $ZnCl_2$:700^oC: 120 min: 1:0.75 (f) Shell: $ZnCl_2$:700^oC: 60 min: 1:0.5

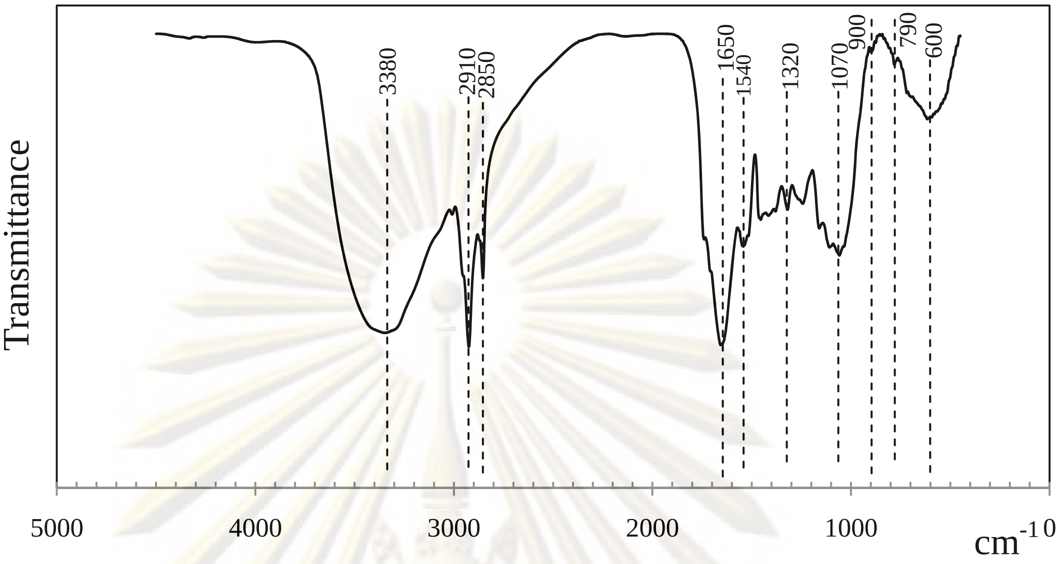

Figure 4.10 FTIR of jatropha seed cake

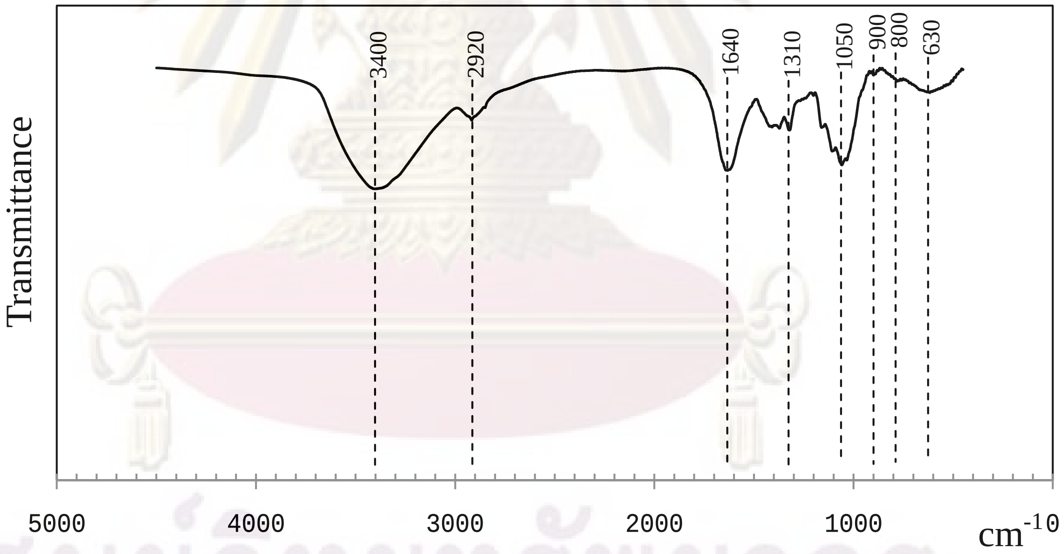

Figure 4.11 FTIR of jatropha shell

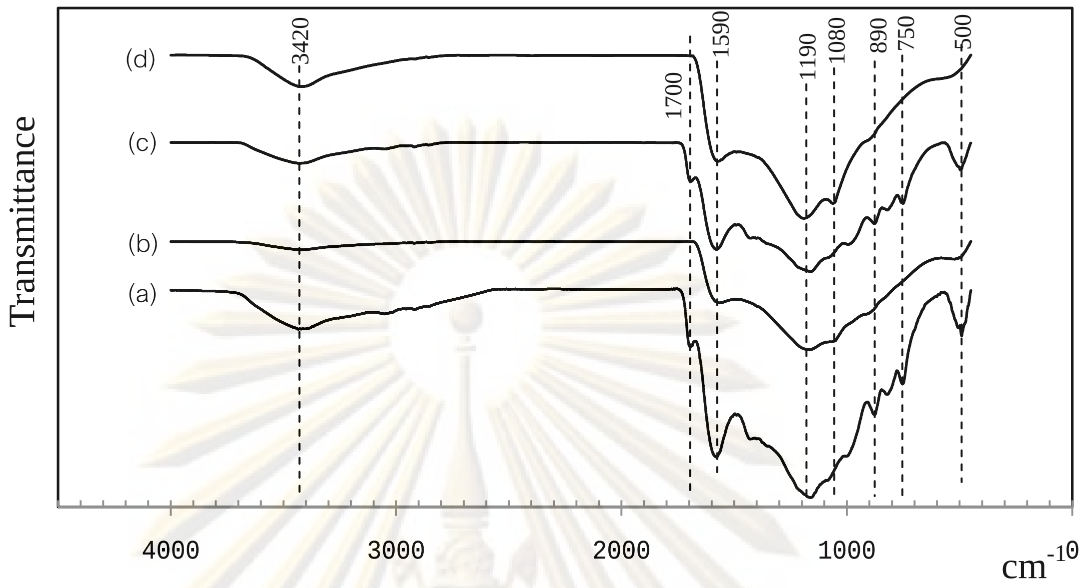

Figure 4.12 FTIR of activated carbon from jatropha seed cake with phosphoric acid activation at: (activation temperature: activation time, and impregnation ratio)

(a) 600^{o}C 60 min, and 1:0.5 (b) 700^{o}C 60 min, and 1:0.5 (c) 700^{o}C 120 min, and 1:0.5 (d) 700^{o}C 120 min, and 1:1

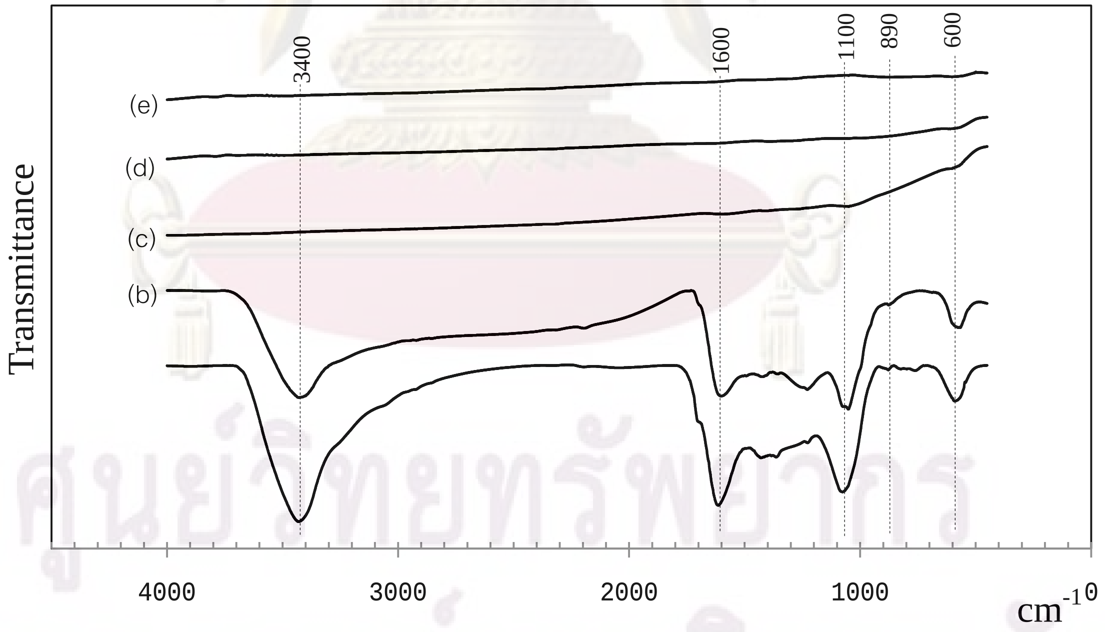

Figure 4.13 FTIR of activated carbon from jatropha seed cake with potassium hydroxide activation at: (activation temperature: activation time, and impregnation ratio)

(a) 600^{o}C 60 min, and 1:0.5 (b) 700^{o}C 60 min, and 1:0.5 (c) 700^{o}C 120 min, and 1:0.5 (d) 700^{o}C 180 min, and 1:0.5 (e) 700^{o}C 180 min, and 1:0.75

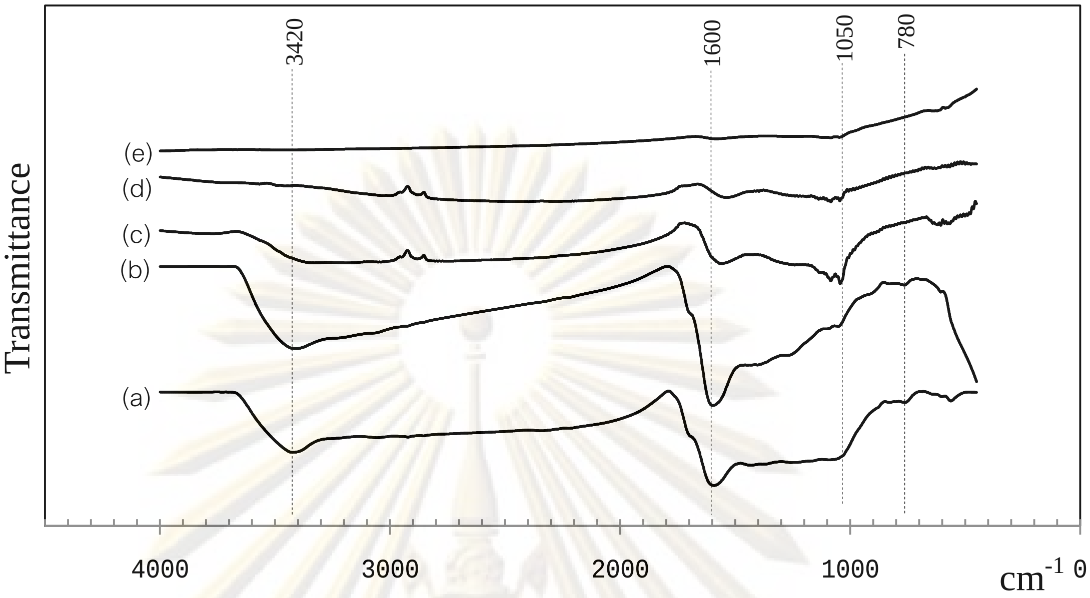

Figure 4.14 FTIR of activated carbon from jatropha seed cake with zinc chloride activation at: (activation temperature: activation time, and impregnation ratio)
(a) 500°C 60 min, and 1:0.5 (b) 600°C 60 min, and 1:0.5 (c) 700°C 60 min, and 1:0.5 (d) 700°C 120 min, and 1:0.5 (e) 700°C 120 min, and 1:0.75

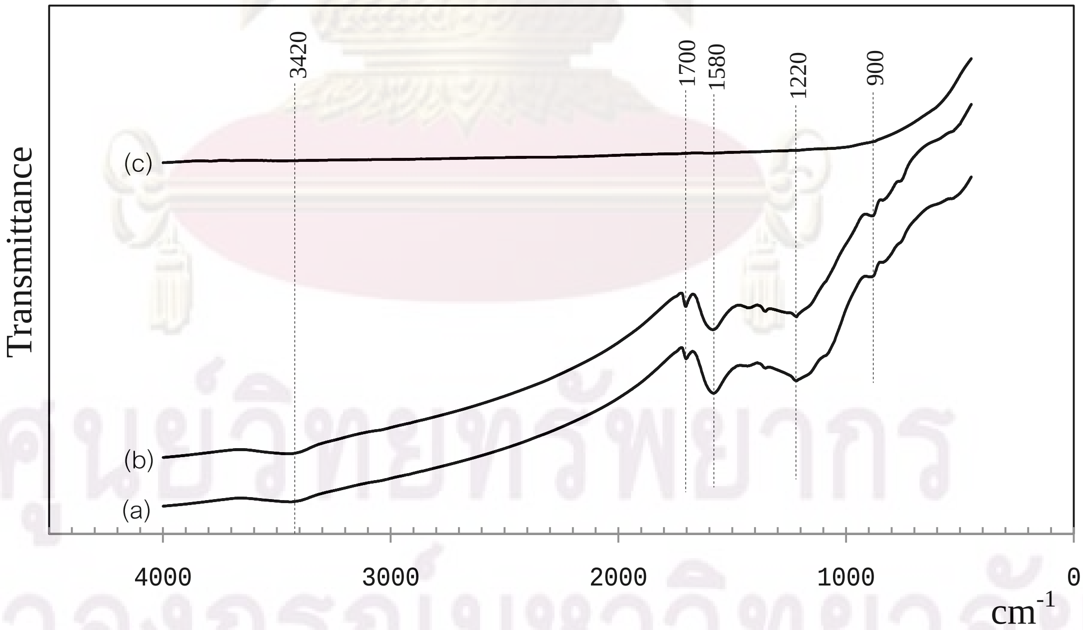

Figure 4.15 FTIR of activated carbon from jatropha shell with phosphoric acid activation at: (activation temperature: activation time, and impregnation ratio)
(a) 500°C 60 min, and 1:0.5 (b) 600°C 60 min, and 1:0.5 (c) 700°C 60 min, and 1:0.5

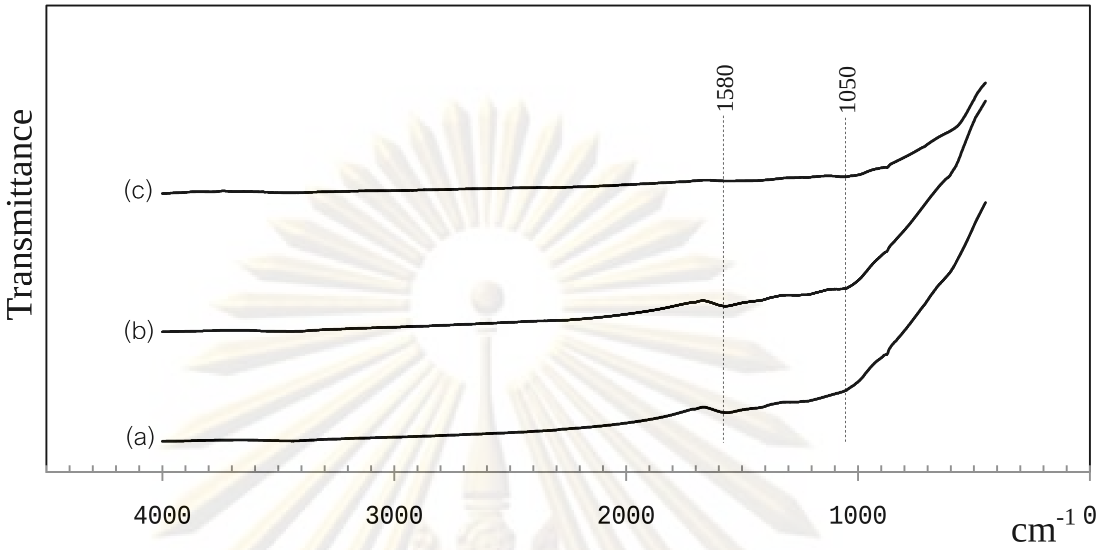

Figure 4.16 FTIR of activated carbon from jatropha shell with potassium hydroxide activation at: (activation temperature: activation time, and impregnation ratio)
(a) 700^{o}C 60 min, and 1:0.5 (b) 700^{o}C 120 min, and 1:0.5 (c) 700^{o}C 120 min, and 1:0.75

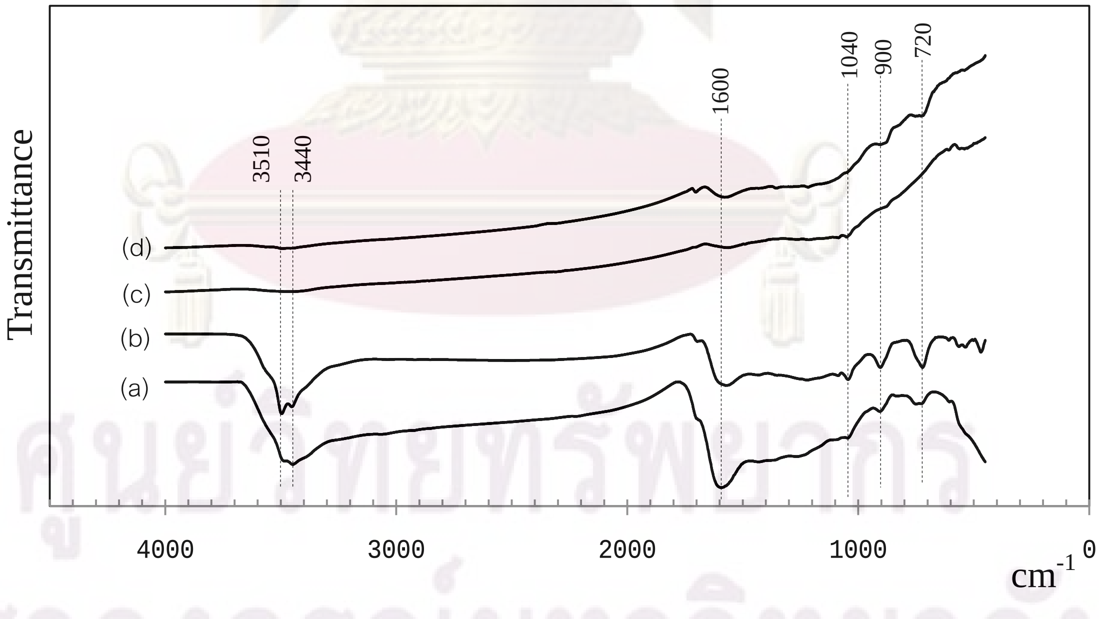

Figure 4.17 FTIR of activated carbon from jatropha shell with zinc chloride activation at: (activation temperature: activation time, and impregnation ratio)
(a) 600^{o}C 60 min, and 1:0.5 (b) 700^{o}C 60 min, and 1:0.5 (c) 700^{o}C 120 min, and 1:0.5
(d) 700^{o}C 60 min, and 1:0.75

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The investigation in this work leads to the following conclusions:

1. Activated carbon prepared from both jatropha seed cake and jatropha shell by KOH as an activating agent exhibited the highest surface area. However, if yield was to be considered for the net iodine number, activated carbon prepared from both jatropha seed cake and jatropha shell with zinc chloride activation exhibited the greatest adsorption properties.
2. The best conditions for production of high surface area activated carbon from jatropha seed cake and shell are the activation with potassium hydroxide; activation temperature of 700^{o}C (for both cake and shell), activation time of 180 (cake) and 60 (shell) minutes, and impregnation ratio between raw material:chemical agent of 1:0.75 (cake) and 1:0.5 (shell). At this optimal condition, the BET surface areas are 666 and 699 m^2/g, respectively and iodine numbers are 696 and 634 mg/g.
3. The best conditions for production of net iodine number from jatropha seed cake and shell are the activation with zinc chloride; activation temperature 700^{o}C (both cake and shell), activation time of 120 minutes (cake) and 60 minutes (shell), and impregnation ratio of 0.5 (cake) and 0.75 (shell). At this optimal condition, the net iodine number is 285 mg/g and 192 mg/g, respectively.

5.2 Contributions

This work reveals the possibility in the use of jatropha waste (after oil extraction) in the production of activated carbon. Several options have been tested for the optimality which was reported in several sections of this thesis. The main contribution obtained from this work is therefore the conditions at which the activated carbon could be best produced from jatropha seed cake and shell. Although the achievement in this work was still limited to small scale conversion, such information could be useful for the future scale up of the future well defined technology.

5.3 Recommendations/Future works

As generally known, chemical activation usually requires the use of hazardous chemicals and always ends up with the wastewater problems that need to be dealt with. Although this work reveals the potential in converting jatropha residue into useful products like activated carbon, the issue of wastewater still has not been addressed. It is therefore recommended that future work should be directed towards the development of cleaner technologies for such conversion. For instance, the recovery of chemicals or water should be considered, and even the use of physical conversion method should be examined in comparison with this chemical technique.

REFERENCES

Alhamed et al. 2009. Sulfur removal from model diesel fuel using granular activated carbon from dates' stones activated by $ZnCl_2$. Fuel 88 (1):87-94.

Aravindhan, R., J. Raghava Rao, and B. Unni Nair. 2009. Preparation and characterization of activated carbon from marine macro-algal biomass. Journal of Hazardous Materials 162 (2-3):688-694.

Aygun et al. 2003. Production of granular activated carbon from fruit stones and nutshells and evaluation of their physical, chemical and adsorption properties. Microporous and Mesoporous Materials 66 (2-3):189-195.

Baaoui, A., A. Yaacoubi, A. Dahbi, C. Bennouna, R. Phan Tan Luu, F. J. Maldonado-Hodar, J. Rivera-Utrilla, and C. Moreno-Castilla. 2001. Optimization of conditions for the preparation of activated carbons from olive-waste cakes. Carbon 39 (3):425-432.

Baccar et al. 2009. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. Journal of Hazardous Materials 162 (2-3):1522-1529.

Bestani, B., N. Benderdouche, B. Benstaali, M. Belhakem, and A. Addou. 2008. Methylene blue and iodine adsorption onto an activated desert plant. Bioresource Technology 99 (17):8441-8444.

Bringi, N. V. 1987. Non-Traditional Oilseeds and Oils in India.Oxford & IBH Publishing Co. Pvt. Ltd., New Delhi.

Budinova et al. 2006. Characterization and application of activated carbon produced by H_3PO_4 and water vapor activation. Fuel Processing Technology 87 (10):899-905.

Budinova, T., N. Petrov, J. Parra, and V. Baloutzov. 2008. Use of an activated carbon from antibiotic waste for the removal of Hg(II) from aqueous solution. Journal of Environmental Management 88 (1):165-172.

Cabal, B., T. Budinova, C. O. Ania, B. Tsyntsarski, J. B. Parra, and B. Petrova. 2009. Adsorption of naphthalene from aqueous solution on activated carbons obtained from bean pods. Journal of Hazardous Materials 161 (2-3):1150-1156.

Carels, N., K. Jean-Claude, and D. Michel. 2009. Chapter 2 Jatropha curcas: A Review. In Advances in Botanical Research: Academic Press, 39-86.

Chandra, T. C., M. M. Mirna, J. Sunarso, Y. Sudaryanto, and S. Ismadji. 2009. Activated carbon from durian shell: Preparation and characterization. Journal of the Taiwan Institute of Chemical Engineers 40 (4):457-462.

Daifullah, A. A. M., B. S. Girgis, and H. M. H. Gad. 2004. A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. Colloids and Surfaces A: Physicochemical and Engineering Aspects 235 (1-3):1-10.

Demirbas, e. a. 2008. Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon. Bioresource Technology 99 (13):5368-5373.

Diao, Y., W. P. Walawender, and L. T. Fan. 2002. Activated carbons prepared from phosphoric acid activation of grain sorghum. Bioresource Technology 81 (1):45-52.

El-Hendawy, A.-N. A. 2009. An insight into the KOH activation mechanism through the production of microporous activated carbon for the removal of Pb2+ cations. Applied Surface Science 255 (6):3723-3730.

Ganan-Gomez, J., A. Maćias-Garćia, M. A. Diaz-Diez, C. Gonzolez-Garcia, and E. Sabio-Rey. 2006. Preparation and characterization of activated carbons from impregnation pitch by $ZnCl_2$. Applied Surface Science 252 (17):5976-5979.

Girgis, B. S., E. Smith, M. M. Louis, and A.-N. A. El-Hendawy. 2009. Pilot production of activated carbon from cotton stalks using H_3PO_4. Journal of Analytical and Applied Pyrolysis 86 (1):180-184.

Gratuito, M. K. B., T. Panyathanmaporn, R. A. Chumnanklang, N. Sirinuntawittaya, and A. Dutta. 2008. Production of activated carbon from coconut shell: Optimization using response surface methodology. Bioresource Technology 99 (11):4887-4895.

Guo, J., and A. C. Lua. 2003. Surface Functional Groups on Oil-Palm-Shell Adsorbents Prepared by H_3PO_4 and KOH Activation and their Effects on

Adsorptive Capacity. Chemical Engineering Research and Design 81 (5):585-590.

Gurses, A., Dogar, S. Karaca, M. Aikyildiz, and R. Bayrak. 2006. Production of granular activated carbon from waste Rosa canina sp. seeds and its adsorption characteristics for dye. Journal of Hazardous Materials 131 (1-3):254-259.

Haimour, N. M., and S. Emeish. 2006. Utilization of date stones for production of activated carbon using phosphoric acid. Waste Management 26 (6):651-660.

Hawash, S., N. Kamal, F. Zaher, O. Kenawi, and G. E. Diwani. 2009. Biodiesel fuel from Jatropha oil via non-catalytic supercritical methanol transesterification. Fuel 88 (3):579-582.

Jibril, B., O. Houache, R. Al-Maamari, and B. Al-Rashidi. 2008. Effects of H_3PO_4 and KOH in carbonization of lignocellulosic material. Journal of Analytical and Applied Pyrolysis 83 (2):151-156.

Kalderis, D., S. Bethanis, P. Paraskeva, and E. Diamadopoulos. 2008. Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. Bioresource Technology 99 (15):6809-6816.

Li, W., J. Peng, L. Zhang, K. Yang, H. Xia, S. Zhang, and S.-h. Guo. 2009. Preparation of activated carbon from coconut shell chars in pilot-scale microwave heating equipment at 60 kW. Waste Management 29 (2):756-760.

Lillo Rodenas, Cazorla-Amor๓s, and Linares-Solano. 2003. Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. Carbon 41 (2):267-275.

Lua, A. C., T. Yang, and J. Guo. 2004. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. Journal of Analytical and Applied Pyrolysis 72 (2):279-287.

Manurung, R., Heeres, H.J., Ratnaningsih, E., Suryatmana, P.,, and M. R. Satyawati, Junistia, L., Daniel, L. 2006. Initial Stage on the Volarisation of Jatropha curcas Using Biorefinery. International Symposium on Volarisation of Indonesian Renewable Resources and Particularly Jatropha curcas Using the Biorefinery Concept, The Agency for the Assessment and Application of Technology, Jakarta November:20-21.

Marsh, H., and F. Rodriguez-Reinoso. 2006. Activated Carbon. In Activated Carbon. Oxford: Elsevier Science Ltd.

Marsh, H., D. S. Yan, T. M. O'Grady, and A. Wennerberg. 1984. Formation of active carbons from cokes using potassium hydroxide. Carbon 22 (6):603-611.

Martin-Gullon, I., J. P. Marco-Lozar, D. Cazorla-Amor๓s, and A. Linares-Solano. 2004. Analysis of the microporosity shrinkage upon thermal post-treatment of H_3PO_4 activated carbons. Carbon 42 (7):1339-1343.

Mozammel, H. M., O. Masahiro, and B. Sc. 2002. Activated charcoal from coconut shell using $ZnCl_2$ activation. Biomass and Bioenergy 22 (5):397-400.

Nakagawa, Y., M. Molina-Sabio, and F. Rodrํguez-Reinoso. 2007. Modification of the porous structure along the preparation of activated carbon monoliths with H_3PO_4 and $ZnCl_2$. Microporous and Mesoporous Materials 103 (1-3):29-34.

Namasivayam, C., D. Sangeetha, and R. Gunasekaran. 2007. Removal of Anions, Heavy Metals, Organics and Dyes from Water by Adsorption onto a New Activated Carbon from Jatropha Husk, an Agro-Industrial Solid Waste. Process Safety and Environmental Protection 85 (2):181-184.

Ncibi, M. C., V. Jeanne-Rose, B. Mahjoub, C. Jean-Marius, J. Lambert, J. J. Ehrhardt, Y. Bercion, M. Seffen, and S. Gaspard. 2009. Preparation and characterisation of raw chars and physically activated carbons derived from marine Posidonia oceanica (L.) fibres. Journal of Hazardous Materials 165 (1-3):240-249.

Okay, O. 2000. Macroporous copolymer networks. Progress in Polymer Science 25 (6):711-779.

Olivares-Marin, M., C. Fernandez-Gonzolez, A. Macias-Garcia, and V. Gomez-Serrano. 2006. Preparation of activated carbon from cherry stones by chemical activation with $ZnCl_2$. Applied Surface Science 252 (17):5967-5971.

Olivares-Marํn, M., J. A. Fernแndez, M. J. Lแzaro, C. Fernแndez-Gonzแlez, A. Macํas-Garcia, V. Gomez-Serrano, F. Stoeckli, and T. A. Centeno. 2009. Cherry stones as precursor of activated carbons for supercapacitors. Materials Chemistry and Physics 114 (1):323-327.

Oliveira, L. C. A., E. Pereira, I. R. Guimaraes, A. Vallone, M. Pereira, J. P. Mesquita, and K. Sapag. 2009. Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents. Journal of Hazardous Materials 165 (1-3):87-94.

Patnukao, P., and P. Pavasant. 2008. Activated carbon from Eucalyptus camaldulensis Dehn bark using phosphoric acid activation. Bioresource Technology 99 (17):8540-8543.

Prahas, D., Y. Kartika, N. Indraswati, and S. Ismadji. 2008. Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization. Chemical Engineering Journal 140 (1-3):32-42.

Qian, Q., M. Machida, and H. Tatsumoto. 2007. Preparation of activated carbons from cattle-manure compost by zinc chloride activation. Bioresource Technology 98 (2):353-360.

Rosas, J. M., J. Bedia, J. Rodríguez-Mirasol, and T. Cordero. 2009. HEMP-derived activated carbon fibers by chemical activation with phosphoric acid. Fuel 88 (1):19-26.

Sahay, K. M., Singh, K.K. 1996. Unit Operation of Agricultural Processing. Vikas Publishing House Pvt. Ltd., New Delhi, India.

Savova, D., E. Apak, E. Ekinci, F. Yardim, N. Petrov, T. Budinova, M. Razvigorova, and V. Minkova. 2001. Biomass conversion to carbon adsorbents and gas. Biomass and Bioenergy 21 (2):133-142.

Srinivasakannan et al. 2004. Production of activated carbon from rubber wood sawdust. Biomass and Bioenergy 27 (1):89-96.

Sutcu, H., and H. Demiral. 2009. Production of granular activated carbons from loquat stones by chemical activation. Journal of Analytical and Applied Pyrolysis 84 (1):47-52.

Tay, T., S. Ucar, and S. Karagoz. 2009. Preparation and characterization of activated carbon from waste biomass. Journal of Hazardous Materials 165 (1-3):481-485.

Temmink, H., and K. Grolle. 2005. Tertiary activated carbon treatment of paper and board industry wastewater. Bioresource Technology 96 (15):1683-1689.

Ucar, S., M. Erdem, T. Tay, and S. Karagьz. 2009. Preparation and characterization of activated carbon produced from pomegranate seeds by $ZnCl_2$ activation. Applied Surface Science 255 (21):8890-8896.

Usmani, T. H., T. W. Ahmad, and A. H. K. Yousufzai. 1994. Preparation and liquid-phase characterization of granular activated-carbon from rice husk. Bioresource Technology 48 (1):31-35.

Wang, X., N. Zhu, and B. Yin. 2008. Preparation of sludge-based activated carbon and its application in dye wastewater treatment. Journal of Hazardous Materials 153 (1-2):22-27.

Yagmur, E., M. Ozmak, and Z. Aktas. 2008. A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. Fuel 87 (15-16):3278-3285.

Yorgun, S., N. Vural, and H. Demiral. 2009. Preparation of high-surface area activated carbons from Paulownia wood by $ZnCl_2$ activation. Microporous and Mesoporous Materials 122 (1-3):189-194.

Youssef, A. M., N. R. E. Radwan, I. Abdel-Gawad, and G. A. A. Singer. 2005. Textural properties of activated carbons from apricot stones. Colloids and Surfaces A: Physicochemical and Engineering Aspects 252 (2-3):143-151.

APPENDICES

APPENDIX A

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^{o}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 ± 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 ± 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)

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

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:

$$A = (N_2)(12693.0) \tag{A.1-2}$$

where N_2 is iodine concentration (N).

$$B = (N_1)(126.93) \tag{A.1-3}$$

where N_1 is sodium thiosulfate concentration (N).

$$DF = \frac{[I+H]}{F} \tag{A.1-4}$$

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.1-1)

$$M = \frac{[A-(DF)(C)(126.93)(50)]}{E} \tag{A.1-5}$$

where C is residual filtrate (N) and E estimated iodine number of the carbon.

for approximation carbon dosage (M) may be use Table A.1-1

Table A.1-1 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
	M				M		
E	C=0.01	C=0.02	C=0.03	E	C=0.01	C=0.02	C=0.03
850	1.329	1.164	1.000	2100	0.538	0.471	00405
900	1.255	1.100	0.945	2150	0.525	0.460	0.396
950	1.189	1.042	0.895	2200	0.513	0.450	0.388
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
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.1-5)

$$C = \frac{(N_1 \cdot S)}{F} \qquad \text{(A.1-6)}$$

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.

APPENDIX B

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 × 30 mesh
2. Dry the activated carbon sample in oven at 150 ^{o}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 ^{o}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/Po)
2. Pass 99.5% 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/Po) and qualities of N_2 that adsorped at the relative pressure [W (P/Po) – 1] - 1 , we can calculated the specific surface area by Eq. (A.3-1)

$$S_{BET}(m^2/g) = \frac{NA_{CS}}{\left[(S+I)(MW)\right]} \qquad \text{(A.3-1)}$$

where : N = Avogrado number (6.02×10^{23} molecule/mole)

A_{CS} = Cross section area of N_2 molecule

MW = Molecular weight of N_2

APPENDIX C

Determination for Ash Content (ASTM D 2866-94)

Apparatus

- *Muffle Furnace*, having air circulation, capable of temperature regulation of ± 25^{o}C at 650 ^{o}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 ^{o}C

Procedure

1. Ignite the crucible in the muffle furnace at 650 ± 25^{o}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 ± 5 ^{o}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 ± 25^{o}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:

$$\text{Total ash,\%} = \frac{(D-B)}{(C-B)} \times 100 \qquad \text{(A.4-1)}$$

where : B = weight of crucible, g

C = weight of crucible plus original sample, g

D = weight of crucible plus ashed sample, g

APPENDIX D

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 ± 5^{o}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:

$$\text{Apparent density, g/mL} = \frac{\text{weight of activated carbon}}{100} \qquad (A.5\text{-}1)$$

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

$$\text{Apparent density, g/mL} = 10^{-4}\,(\text{weight of activated carbon,g}) \times (100 - \%\ \text{moisture}) \qquad (A.5\text{-}2)$$

APPENDIX E

Determination for Moisture Content (ASTM D 2867-95)

1). <u>Oven-Drying Method</u>

Apparatus

- *Moisture Oven*-Most commercial, electrically heated, forced-circulation drying ovens capable of temperature regulation between 145 ^{o}C and 155 ^{o}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 ^{o}C to 155 ^{o}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:

$$Moisture, weight\% = \frac{(C-D)}{(C-B)} \times 100 \qquad \text{(A.6-1)}$$

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). <u>Xylene-Extraction Method</u>

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^3, 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 abount 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).

Calculation

- Calculate the moisture content as follows:

$$Moisture, weight\% = \frac{V}{(C-E)} \times 100 \qquad \text{(A.6-2)}$$

where : V = water collected, mL

C = initial weight of sample bottle, g

E = weight of sample bottle after removing moisture sample, g

APPENDIX F

Determination for Chemical Analysis (ASTM D 1762-84)

Apparatus

- *Mill,* for grinding samples
- *Oven,* with automatic temperature control at $105 \pm 1\ ^{o}C$
- *Muffle Furnace,* to control temperature at $750 \pm 5\ ^{o}C$ and $950 \pm 5\ ^{o}C$
- *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-μm) 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-μm) sieve. These fine particles contribute to errors of being awept 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-μm) 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:

$$Moisture,\% = \frac{(A-B)}{A} \times 100 \tag{A.7-1}$$

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:

$$Volatile-matter,\% = \frac{(B-C)}{B} \times 100 \tag{A.7-2}$$

where : C = grams of sample after drying at 950 ^{o}C

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

$$Ash,\% = \frac{D}{B} \times 100 \qquad \text{(A.7-3)}$$

where : D = grams of residue

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

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

APPENDIX G

Paper Publication (Conference Article)

Wichanon Watsanathip, Vorapot Kanokkantapong, Prasert Pavasant. **Preparation of activated carbon from Jatropha wastes via phosphoric acid chemical activation.** 2009. The 19th Thailand Chemical Engineering and Applied Chemistry Conference October 26-27, 2009, Kanchanaburi Thailand.

BIOGRAPHY

Name : Wichanon Watsanathip
Date of Birth : January 14, 1986
Place of Birth : Kanchanaburi, Thailand
Institution Attended : Sarasit Phittayalai School, Ratchaburi, Thailand
Certificate of Mathayomsuksa 6
Department of Chemical Engineering,
Faculty of Engineering and Industrial Technology,
Silpakorn University, Nakornpathom, Thailand
Bachelor’s Degree of Engineering