TO PRODUCE THE ACTIVATED CARBON FROM MATURED PALM KERNEL SHELL

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**A thesis submitted in fulfillment
of the requirements for the award of the Degree of
Bachelor of Chemical Engineering (Chemical)**

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NOVEMBER 2010

ABSTRACT

The objectives of this experiment were to prepare the activated carbon from matured palm kernel shell as a raw material by carbonization and the studied which optimum variables such as temperature, concentration of phosphoric acid and cooling down time are suitable. Activated carbon is a form of carbon that has been processed to make extremely porous and have very large surface area for adsorption and chemical reactions. The matured palm kernel shell is carbonized in a glass furnace at elevation temperature after soaked with H_3PO_4 acid and cooled down the carbonized activated carbon. Methyl orange are used as an indicator to test the carbonized raw material whether it is activated carbon or common charcoal. The real activated carbon would change the orange solution to a clear solution and the solution of different color is analyzed by using FTIR to check the functional group of methyl orange. The result showed that 1000^oC is the optimum temperature to carbonize the raw material and the use of 0.35M H_3PO_4 acid with the cooling down time at 30 minutes would give the best adsorption of activated carbon after filtration. From the data obtained by FTIR, the 0.35M H_3PO_4 acid has showed that the peak functional group of methyl orange is reduced from first filtration till last filtration. It is recommend that the raw material not to be crushed small than 0.2 mm, because it will effect the adsorption and filtration rate. As a conclusion, The activated carbon has been produced from matured palm kernel shell using glass furnace and The optimum effect of variables have been determined by observation and analysis of FTIR, it is at 1000^0C of temperature, by impregnated in 0.35M of Phosphoric acid and cool the activated carbon down in 30 minutes are found to be the optimum variables in producing the activated carbon.

ABSTRAK

Objektf untuk eksperimen ini adalah untuk menyediakan karbon teraktif dari tempurung kelapa sawit sebagai bahan mentah melalui proses karbonisasi dan untuk mengkaji pemboleh ubah optimum yang sesuai seperti suhu, kepekatan asid fosforik dan masa penyejukan. Karbon teraktif adalah suatu bentuk karbon yang telah di proses untuk menjadikannya berpori dan mempunyai luas permukaan yang sangat besar untuk tindak balas jerapan dan kimia. Tempurung kelapa sawit di karbonisasikan tungku kaca pada suhu yang tinggi setelah di rendam di dalam asid fosforik (H_3PO_4) dan karbon teraktif yang di karbonisasi di sejukkan. Metil jingga digunakan sebagai penunjuk untuk menguji bahan mentah yang terkarbonisasi itu karbon teraktif atau arang biasa. Karbon teraktif akan mengubah cecair oren kepada cecair jernih dan cecair tersebut akan dianalisa dengan menggunakan FTIR untuk menyemak kumpulan berfungsi metil jingga. Keputusan kajian telah menunjukkan bahawa 1000^oC adalah suhu optimum untuk mengkarbonisasi bahan mentah dan perendaman di dalam 0.35M asid fosforik dangan masa penyejukkan 30 minit akan memberikan jerapan karbon teraktif terbaik selepas penapisan. Dari data yang diperoleh oleh FTIR, asid fosforik 0.35M menunjukkan bahawa kumpulan berfungsi metal jingga berkurang dari penapisan pertama sampai terakhir. Disarankan bahawa bahan mentah tidak dihancurkan kurang dari 0.2mm kerana akan mempengaruhi keberkesanan kadar jerapan dan penapisan. Secara kesimpulannya, karbon teraktif yang telah dihasilkan dari tempurung kelapa sawit dengan menggunakan tungku kaca dan kesan pemboleh ubah yang optimum telah ditentukan oleh pemerhatian dan analisis FTIR, ialah pada suhu 1000^oC yang direndam dengan 0.35 asid fosforik dan 30 minit masa untuk penyejukkan dalam menghasilkan karbon teraktif.

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LIST OF ABBREVIATIONS

AC	ACTIVATED CARBON
PKS	PALM KERNAL SHELL
FTIR	FOURIER TRANSFORM INFRARED

LIST OF SYMBOL

^{0}C	Degree Celcius
Min	Minute
M	Molar

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, the development of the oil palm industry has influenced the production of by products at plantation grounds, oil mills and refineries. Department of Statistics of Malaysia, Statistics of Oil Palm, Coconut, Tea and Cocoa (1981) estimated that processing produced annually about 2.52 million tones of palm mesocarp fiber, 1.44 million tones of oil palm shells and 4.14 million tones of empty fruit bunches as waste. It is an added advantage to the oil palm industry if this biomass can be turned into useful and valuable products. According to the statistics, about 1120 kg of oil palm shells are produced per hectare of oil palm planted area (A.H. Shamsudin-1985). The characteristic of palm kernel shell such as fixed carbon, ash content and high carbon but low inorganic contents in oil palm shell shows that it is suitable for palm kernel shell use as a raw material for activated carbon (AC) production. Palm kernel shell is one of local agriculture product that is inexpensive and easy to get. It is important to note that the raw material quality has very large influence on the characteristics and performance of activated carbon. A number of researches have been reported in the literature using other agriculture products as raw materials. Table 1.1 summarizes various works with reference to the raw materials using, methods and their application of activated carbon produced.

Table 1.1 Summary of earlier work on activated carbon using other agriculture products

Authors	Year	Raw materials	Method	Application
Luo and Guo	2001	Oil palm stones	CO2 activation	SO2 removal
Hu and Srivinasan	2001	Coconut shell	ZnCl2 activation and CO2 activation	Phenol, methylene blue
Mozammel et al.	2002	Coconut shell	ZnCl2 activation	Iodine
Hu et al.	2001	Coconut shell and palm seed	ZnCl2 activation	Phenol and dye
Daun and All	2004	Coconut shell	Physical activation (N2 gas)	Nitrogen adsorption

Activated carbon, also called activated charcoal or " Activated coal" is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions (Hasler-1974). The activated carbon has the strongest physical adsorption forces of the highest volume adsorbing porosity of any material known to mankind (Lua & Guo-2001). By now, a lot of research has been done on activated carbon to improve the application of activated carbon. One of the fastest growing areas is in environmental applications such as wastewater treatment. In the treatment of wastewater, it is used for purification, decolorization and the removal of toxic organics and heavy metal ions due to adsorption process. Adsorption can be defined as a surface process by which adsorbate molecules accumulate from an ambient fluid phase on the active sites of adsorbent and lose their kinetic energies, making the process exothermic (Rodriguez-Reinoso and Lanires-

Solano- 1965). The adsorption capability of activated carbon can be applied to remove large variety of compound from contaminated water through carbon adsorption. Recently, researches have been focused more on removal of heavy metal ions such as cooper, zinc and chromium, mercuryand cyanide. Besides, carbon adsorption is a widely used method of home water filter treatment because of its ability to improve water by removing disagreeable tastes and odors.

1.2 Problem Statement

Extracted mesocarp fiber (or exocarp) and fruit shell (or endocarp) are two major solid wastes from oil palm mills. In Malaysia, the largest oil palm producer in the world, about two million tones (dry weight) of shell and one million tones of extracted fiber are generated annually. This is has proved that the abundance of biomass from oil palm industry make the oil palm shell easy to obtain and use as raw material for activated carbon production. The processing method is one of the factor that the research should be done. Before this, the processing method of activated carbon production was not use the acidic solution to loose the fiber and traces by soaking the raw material. This is important to increase the surface area of activated carbon.

Nowadays, the resources of hardwood are become limited and the hardwood cost is very expensive. Hence, the oil palm shell can be the alternative raw material to replace the hardwood to produce the activated carbon. Besides, the environment can be protected from global warming effect due to logging activities. Furthermore, the activated carbon can be used in water filtration system through carbon adsorption in order to get clean water to mankind. This is because the activated carbon has higher adsorption capacity to adsorb color, taste, odor, chemicals (Cd, Pb and Cr) and heavy metal (Mg and K) due to its tendency of interaction of elements on the surface of activated carbon.

1.3 Objective

The objectives of this project are:

i. To prepare the activated carbon from matured oil palm shell by carbonization.
ii. To study which effect of variables such as temperature, concentration of H_3PO_4 acid and cooling down time optimum and suitable on the activated carbon preparation.

1.4 Scope of Research

There are some important tasks to be carried out in order to achieve the objective of this study. The important scopes have been identified for this research in achieving the objective:

i. In this study, different concentrations of H3PO4 acid are being used to provide wide of surface area of activated carbon.
ii. In this research, different temperature elevation is used, to predict the optimum temperature in producing activated carbon.
iii. The different cooling down time is being used to select the optimum time for cooling down the activated carbon after carbonization.
iv. In this experiment, the methyl orange solution as an indicator to determine the carbonized raw material is activated carbon or not.
v. The filtered methyl orange solution by using prepared activated carbon (concentrations of H3PO4 acid effect) is analyzed by using Fourier Transform Infrared (FTIR).

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1.5 Rationale & Significance

The rationale and significance of this research can be classified into 3 terms, there are:

i. Usage of Biomass/waste to wealth project

The abundance of biomass from oil palm industry has contributed the chance to implement 'waste to wealth' project. By using the biomass of oil palm we can reduce the by product from oil palm plantations, mills and refineries.

ii. Process Method

The already process method has improve the quality of the activated carbon by increase the surface area of activated carbon.

iii. Nature & Environment

The production of activated carbon can reduce the polluted water by carbon adsorption in water filtration in order to get clean water. Besides, the logging activities (to obtain hardwood as raw material), that will give global warming effect, can be reduced by replacing with oil palm shell.

iv. Economy

The availability of oil palm shell in abundance make it easy to get and cheap in market. By reuse this by product, the profit of the company can be doubled and 'waste to wealth' project can be implemented.

v. Effectiveness

The activated carbon produced is effective in quality and cost. This is because the method to produce it is easy to handle.

CHAPTER 2

LITERATURE REVIEW

2.1 Oil Palm Kernel Shell

In oil palm industry, oil palm is produced in 42 countries worldwide on about 27 million acres. Average yields are 10,000 lbs/acre, and per acre yield of oil from African oil palm is more than 4-fold that of any other oil crop, which has contributed to the vast expansion of the industry over the last few decades.

Table 2.2 Top 10 Countries (% of world production)

Top 10 Countries (% of world production)	
1. Malaysia (44%)	6. Cote d'Ivoire (1%)
2. Indonesia (36%)	7. Ecuador (1%)
3. Nigeria (6%)	8. Cameroon (1%)
4. Thailand (3%)	9. Congo (1%)
5. Colombia (2%)	10. Ghana (1%)

Based on the above table, Malaysia is amongst the world's top producers of palm oil with the current planted area is expanding to around 4.5 million hectares. This is has proved that the abundance of oil palm that will produce large quantity of biomass of oil palm. The biomass of oil palm can be reuse by adding the additive that will produce good value added product. One of example of oil palm biomass is oil palm kernel shell (endocarp).

The oil palm kernel shell can be consumed in the production of activated carbon. The selection of oil palm kernel shell to produce the activated carbon must be selected by it's thickness of shell; endocarp. Besides, the oil palm kernel shell must be obtained from 8 years old oil palm trees to ensure that the endocarp is thick enough. The endocarp is varying in thickness, with *dura* types having thick endocarps and less mesocarp, and *tenera* types the opposite. By choosing the *dura* types of oil palm kernel shell, the activated carbon can be better in quality. By using these oil palm biomass, the profit for the producer of oil palm industry can be doubled and directly generate Malaysia economy.

Below are the characteristics of oil palm origin that contribute the selection of oil palm kernel shell.

Table 2.2 Characteristics of *Dura* oil palm types

Features	**Percentage**
Mesocarp	20-65%
Shell thickness	20-50%
Seed thickness	4-20%

Table 2.3 Characteristic of *Tenera* oil palm types

Features	**Percentage**
Mesocarp	60-96%
Shell thickness	3-20%
Seed thickness	3-15%

Fig. 1: Oil Palm Kernel Shell

Fig. 2: *Dura* Oil Palm Fruit

2.2 Activated Carbon

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

Activated carbons have been explained in different way of definition from several authors and this will provide a basis understanding of activated carbons as solid carbon materials. An appreciation of the fine structure of activated carbons leads to an account of the surface forces in pores that give rise to the powerful adsorptive properties of activated carbons. They can be prepared from a large number of raw materials, especially agro-industrial by-products like palm kernel shells by one of the following process; physical reactivation and chemical activation.

2.2.1 Physical reactivation

The process when the precursor is developed into activated carbon using gases (Encinar, Beltran and Ramiro-1988). This is generally done by using one or a combination of the following processes:

(i) Carbonization; material with carbon content is pyrolyzed at temperatures in the range 600-900 °C, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)

(ii) Activation/oxidation; raw material or carbonised material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600-1200 °C.

2.2.2 Chemical activation

Prior to carbonization, the raw material is impregnated with certain chemicals. The chemical is typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, zinc chloride, respectively). Then, the raw material is carbonized at lower temperatures (450-900 °C). It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. This technique can be problematic in some cases, because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

2.2.3 Factors Affecting Activated Carbon Production

1) Raw material

Most organic materials rich in carbon that do not fuse upon carbonization can be used as raw material for the manufacture of activated carbon. The selection of raw material for preparation of porous carbon, several factors are taken into consideration. The factors are:

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

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

Raw materials such as coconut shell and fruit stones are very popular for many types of activated carbon, because their relatively high density, hardness and volatile content are ideal for production of hard granular activated carbon. Coconut shells, together with peach and olive stones are used commercially for the production of microporous activated carbons, useful for a very wide range of applications. Further details about characteristic of raw materials used for making activated carbon are listed in Table 2.4.

Table 2.4 Characteristics of various conventional raw materials used for making AC

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

2) Temperature

Temperature, particularly the final activation temperature, affects the characteristic of the activated carbon produced. Generally, for commercial activated carbon usually conducted at temperature above 800^0C in a mixture of steam and CO_2. Recently, the researches have been working out on optimizing the final activation temperature to economize the cost of production and time. Recently, the researches have been working out on optimizing the final activation temperature to economize the cost of production and time. As reported by several authors, activation temperature significantly affects the production yield of activated carbon and also the surface area of activated carbon. The temperature used as low as 200°Cand up high to 1100°C.

The optimum temperatures have been reported to be between 400°C to 500°C by most the earlier researchers irrespective of the time of activation and impregnation ratio for different raw material. The increasing of activation temperature reduces the yield of the activated carbon continuously. According to Guo and Lua (2001), this is expected since an increasing amount of volatiles is released at increasing temperature from 500°C to 900°C. The decreasing trend in yield is paralleled by the increasing activation temperature due to the activation reaction. These phenomena are also manifested in the decreasing volatile content and increasing fixed carbon for increasing activation temperature. Previously, it is suggested that the percentage of volatile matter decreased with an increased of carbonization temperature and the variation of this parameter was maximum between 200°C and 800°C due to rapid carbonization occurring in this region. It is also unsuitable to prepare activated carbon when carbonization temperature was more than 800°C since the successive decreased in volatile matter is minimal above this range.

This was accompanied with an increased of fixed carbon and ash content which may be attributed to the removal of volatile matter in the material during carbonization process. Thus, leaving behind the more stable carbon and ash-forming minerals. Another notable feature that showed the effect of activation temperature on the activated carbon properties is the BET surface area. As the activation temperature increased, the

BET surface area also increased. This may be attributed to the development of new pores as a result of volatile matter released and the widening of existing ones as the activation temperature become higher.

3) Activation time

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

2.2.4 Definition of Activated Carbon

As all know that Activated carbon is a solid, porous, black carbonaceous material and tasteless. Other definition for activated carbon that define by Ain (2007) is a porous carbon material, usually chars, which have been subjected to reaction with gases during or after carbonization in order to increase porosity. AC is distinguished from elemental carbon by the removal of all non-carbon impurities and the oxidation of the carbon surface.

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

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

2.2.5 Characterization of Activated Carbon

It is very important to characterize the activated carbon in order to classify it for specifics uses. Generally, physical properties and chemical properties are the characteristic of activated carbon. The characteristics of activated carbon depend on the physical and chemical properties of the raw materials as well as activation method used as mentioned by Guo and Luo (2001).

Physical properties of activated carbon, such as ash content and moisture content can affect the use of a granular AC and render them either suitable or unsuitable for specific applications. While the specific surface area of activated carbon and surface chemistry is classified as chemical properties. Furthermore, the porous structure of activated carbon also can be characterize by various techniques such as adsorption of gases(N2, Ar, Kr, CO2) or vapors (benzene, water), scanning electron microscopy(SEM) and transmission electron microscopy (TEM).

2.2.5.1 Ash content

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

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

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

2.2.5.2 Moisture content

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

2.2.5.3 Surface area

Generally, the larger the specific surface area of the adsorbent, the better its adsorption performance will be (Guo and Lua, 2003). The most widely used commercial active carbons have a specific surface area of the order of 600- 1200 m2/g (Ng et.al, 2002). The pore volume limits the size of the molecules that can be adsorbed whilst the surface area limits the amount of material which can be adsorbed, assuming a suitable molecular size. The adsorptive capacity of adsorbent is related to its internal surface area and pore volume. The specific surface area (m2/g) of porous carbon is most usually determined from gas adsorption measurement using the Brunauer-Emmett-Teller BET theory. The most commonly employed method to characterize these structural aspects of the porosity is based on the interpretation of adsorption isotherm (e.g., N_2 at 77K). Nitrogen at its boiling point of 77K is the recommended adsorptive, although argon at 77K also used.

2.2.5.4 Surface Functional Group of Activated Carbon

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

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