

UNIVERSITI MALAYSIA PAHANG

BORANG PENGESAHAN STATUS TESIS[♦]

JUDUL : EFFECT OF SULPHURIC ACID CONCENTRATION ON OIL PALM
EMPTY FRUIT BUNCH (EFB) TO PRODUCE ADVANCED CARBON
PRODUCT

SESI PENGAJIAN : 2011/2012

Saya SITI NURUL AISHAH BT AHMAD NORDIN

(HURUF BESAR)

mengaku membenarkan tesis (~~PSM/Sarjana/Doktor Falsafah~~)* ini disimpan di Perpustakaan Universiti Teknologi Malaysia dengan syarat-syarat kegunaan seperti berikut :

1. Tesis adalah hakmilik Universiti Malaysia Pahang.
2. Perpustakaan Universiti Malaysia Pahang dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.

4. **Sila tandakan (✓)

SULIT (Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)

TERHAD (Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

TIDAK TERHAD

Disahkan oleh

(TANDATANGAN PENULIS)

(TANDATANGAN PENYELIA)

Alamat Tetap No. 33, Perumahan
Jubakar Pantai,
16200, Tumpat, Kelantan

TN HJ MOHD NOOR BIN NAWI
Nama Penyelia

Tarikh : 19 JANUARY 2012

Tarikh: 19 JANUARY 2012

EFFECT OF SULPHURIC ACID
CONCENTRATION ON OIL PALM EMPTY FRUIT
BUNCH (EFB) TO PRODUCE ADVANCED
CARBON PRODUCT

SITI NURUL AISHAH BT AHMAD NORDIN

DEGREE OF BACHELOR OF CHEMICAL
ENGINEERING
UNIVERSITI MALAYSIA PAHANG

We certify that the thesis entitled “Effect of Sulphuric Acid Concentration on Oil Palm Empty Fruit Bunch (EFB) to produce advanced Carbon Product” written by SITI NURUL AISHAH BT AHMAD NORDIN. We have examined the final copy of this thesis and in our opinion; it is fully adequate in term of scope and quality for the award of the Degree in Chemical Engineering. We herewith recommended that it be accepted in fulfillment for the requirements for the degree of Bachelor of Chemical Engineering.

Name of external examiner

Signature

Institution:

Name of internal examiner

Signature

Institution:

EFFECT OF SULPHURIC ACID CONCENTRATION ON OIL PALM EMPTY FRUIT
BUNCH (EFB) TO PRODUCE ADVANCED CARBON PRODUCT

SITI NURUL AISHAH BT AHMAD NORDIN

Thesis submitted in fulfillment of the requirements
for the award of the degree
in Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering

Signature:

NAME OF SUPERVISOR:

POSITION:

DATE:

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature:

NAME:

ID NUMBER:

DATE:

*Special dedication to my mum and dad that always inspire, love and stand beside me,
and to my beloved friend.*

Thank you for all your love, care and support.

ACKNOWLEDGEMENT

Alhamdulillah, praise to ALLAH SWT for His helps and guidance that I finally able to complete this Undergraduate Research Project (URP).

I would like to thank my supervisor Mr Mohd Noor Bin Nawawi for his willingness in overseeing the progress of my project assignments from its initial phases till the completion of it. I thank him for his patience in reviewing my work that helped me to improve my research contributions. I appreciate his help in guiding me to overcome my research and other problems.

Special thanks to my beloved campus, University Malaysia Pahang, especially to Faculty of Chemical & Natural Resources Engineering, for facilities provided during the execution of this research project. To all supporting staffs of the faculty and laboratory assistants, thank you.

I would sincerely thanks to my roommates for their encouragement and also my dad Mr. Ahmad Nordin, my mom Mdm. Rahimah, my sister and brothers and my special friends Md, Rasyidi Bin Mohd Sidek for their prayers, love, encouragement and support right from the beginning because this work would not have been possible without them. I appreciate their sacrifice, patient and morale support throughout my research.

Finally, I pray and thank ALLAH for all.

ABSTRACT

Oil palm empty fruit bunch (EFB) contains polymeric lignocellulosic component such as hemicellulose, cellulose and lignin and is therefore a potential raw material for producing advanced materials such as carbon electrode, and molecular sieve carbon. The parameters that have been focused throughout this experiment were concentration of acid sulphuric and temperature of carbonization. The experimental works has been done at GAS LABORATORY, Universiti Malaysia Pahang (UMP). In this research, the experiment has been run in slow pyrolysis process where empty fruit bunch (EFB) was pre-carbonized at 280 °C, then, it followed by grinding and sieving of the pre-carbonize EFB. Then carbon precursor was treated with 0.2M, 0.4M, and 0.6M of H₂SO₄ and was dried. The chemical changes of the treated EFB carbon precursor were discuses by using the thermogravimetric (TGA) analysis results. The green pellets are then prepare by mould compression of the carbon precursor powder and then will carbonize with 600°C, 800°C, and 1000°C of temperature by using multiple heating profile under nitrogen flow. Carbon pellet that prepared from 0.6 M of H₂SO₄ gave highest density (ρ). Air mixing and high temperature expose to the carbon pellet during carbonization process was affected the properties of carbon pellet, thus advanced carbon product such as carbon electrode and molecular sieve carbon can't be prepared.

ABSTRAK

Tandan kosong sawit (EFB) mengandungi komponen lignocellulosic polimerik seperti hemiselulosa, selulosa dan lignin dan adalah satu bahan mentah berpotensi untuk menghasilkan bahan termaju seperti elektrod karbon, dan karbon ayak molekul. Parameter yang akan dikaji dalam eksperimen ini ialah iaitu kepekatan asid sulfurik dan suhu karbonisasi. Kajian telah dijalankan dalam makmal gas, Universiti Malaysia Pahang (UMP). Dalam kajian ini, eksperimen telah dijalankan dalam proses pirolisis perlahan di mana tandan buah kosong (EFB) di pra-karbonkan pada suhu 280°C, kemudian diikuti dengan mengisaran dan pengayakan karbon precursor. Kemudian prekursor karbon dirawat dengan 0.2M, 0.4M dan 0.6M molar acid sulphuric dan dikeringkan pada suhu bilik. Perubahan kimia prekursor karbon EFB yang telah dirawat dianalisis dengan menggunakan thermogravimetric (TGA). Pelet hijau dihasilkan dengan mampatan acuan dan akan dikarbonisasi dengan suhu 600°C, 800°C dan 1000°C menggunakan profil pemanasan berganda di bawah aliran nitrogen. Pelet karbon yang dirawat dengan kepekatan asid sulfurik 0.6 Molar memberi kepadatan tertinggi (ρ). Pencampuran udara dan suhu tinggi semasa proses pengkarbonan telah menjejaskan sifat pellet karbon, maka produk karbon seperti elektrod karbon dan ayak molekul karbon tidak boleh dihasilkan.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	SUPERVISOR'S DECLARATION	iv
	STUDENT'S DECLARATION	v
	DEDICATION	vi
	ACKNOWLEDGEMENTS	vii
	ABSTRACT	viii
	ABSTRAK	ix
	TABLE OF CONTENTS	x
	LIST OF TABLE	xv
	LIST OF FIGURES	xvi
	LIST OF ABBREVIATIONS	xviii
	LIST OF APPENDICES	xix
1	INTRODUCTION	
	1.1 Background of Study	1
	1.2 Problem Statement	7

1.3	Research Objective	8
1.4	Research Scope	8
1.5	Rationale & Significance of study	9
2	LITERATURE REVIEW	
2.1	Acid Activation	10
2.2	Porosity and surface area	12
2.3	Separation process	16
3	METHODOLOGY	
3.1	Background	23
3.2	Material/Apparatus/Equipment	24
3.3	Method/Procedure/Preparation	24
3.3.1	Flowchart of producing carbon electrode and molecular sieve carbon	24
3.3.2	Dried Empty Fruit Bunch	26
3.3.3	Pre – Carbonization of Empty Fruit Bunch	27

3.3.4	Grinding and Sieving of Empty Fruit Bunch	28
3.3.5	Treated of Empty Fruit Bunch with Sulphuric Acid	29
3.3.6	Molding of the treated carbon	30
3.3.7	Carbonization process	31

4 RESULT AND DISCUSSION

4.1	Introduction	32
4.2	Nitrogen calculation	33
4.3	Pre- carbonization process	34
4.3.1	Heating profile for pre- carbonization process	34
4.3.1.1	Summary for the overall pyrolysis	39
4.4	Effect H ₂ SO ₄ toward carbon precursor	40
4.4.1	Molarity of Sulphuric Acid	40
4.4.2	Characterizations using FTIR	42

4.4.3	Characterization using TGA	45
4.4.3.1	Carbon precursor treated with 0.2M	45
4.4.3.2	Carbon precursor treated with 0.4M	46
4.4.3.3	Carbon precursor treated with 0.6M	47
4.4.4	Physical properties	49
4.4.4.1	Calculation of bulk density of carbon pellet.	49
4.4.4.2	Before Carbonization	50
4.4.4.2	After Carbonization	51

CHAPTER	TITLE	PAGE
4	CONCLUSION	
	5.1 Conclusion	53
	5.2 Recommendation	55
	REFERENCES	56
	APPENDIX A	58

LIST OF TABLES

TABLE NO.	TITLE	PAGE
4.1	1 st pyrolysis	35
4.2	2 nd pyrolysis	35
4.3	3 rd pyrolysis	36
4.4	4 th pyrolysis	37
4.5	5 th pyrolysis	37
4.6	6 th pyrolysis	38
4.7	Summary for the overall pyrolysis	39
4.8	Density of the sample before and after carbonization	49
4.9	Weight (W), Thickness (T), Diameter (D), density (ρ) of the untreated sample (0M), treated sample (0.2M, 0.4M, 0.6M).	50

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Empty Fruit Bunch	2
1.2	Carbon Powder	4
2.1	Porosity and surface area	13
2.2	Process of separation of gases, (O ₂ / N ₂)	17
2.3	Separation of O ₂ and N ₂	17
3.1	Flow chart of producing carbon electrode and molecular sieve carbon	25
3.2	Dried Empty Fruit Bunch	26
3.3	Pre – Carbonization of Empty Fruit Bunch	27
3.4	Grinding and Sieving of Empty Fruit Bunch (Carbon Pre-cursor)	28
3.5	a) Treated of Empty Fruit Bunch with Sulphuric acid	29
	b) Treated carbon drying overnight at room temperature	29
3.6	Molding of the treated carbon	30
3.7	Carbonization process	31

FIGURE NO.	TITLE	PAGE
4.1	Nitrogen Gasses flow into the furnace	33
4.2	FTIR analysis for 0.2M of acid sulphuric	42
4.3	FTIR analysis for 0.4M of acid sulphuric	43
4.4	FTIR analysis for 0.6M of acid sulphuric	43
4.5	TGA analysis for 0.2M of acid sulphuric	45
4.6	TGA analysis for 0.4M of acid sulphuric	46
4.7	TGA analysis for 0.6M of acid sulphuric	47
4.8	Graph of density versus Concentration for before carbonization	50
4.9	Graph of density versus Concentration for after carbonization	51

LIST OF ABBREVIATIONS

AC	-	Activated Carbon
CMS	-	Carbon Molecular sieve
EFB	-	Empty Fruit Bunch
FTIR	-	Fourier Transformation Infra-red Spectroscopy
GAC	-	Granular Activated Carbon
GHG	-	Greenhouse Gas Emissions
MPOB	-	Ministry Palm Oil Board
MSC	-	Molecular Sieve Carbon
PAC	-	Powdered Activated Carbon
PSA	-	Pressure Swing Adsorption
SACG	-	Self-Adhesive Carbon Grain
TGA	-	Thermogravimetric analysis

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Gantt chart / Project Schedule	58

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Malaysia is one of the world leading producers of palm oil with the oil palm plantations produce an average of 18.9 tonnes/hectare of fresh fruit bunches (FFB) in year 2003 (MPOB, 2004). Oil Palm empty fruit bunch (EFB) is a waste material produced in large quantities (15m mt/yr) by palm oil mills (MPOB 2010). The estimated annual total of EFB produced in Malaysia is about two million tones dry weight (Sha'ari et al. 1991). At present EFB are used as mulches and organic fertilizer (Rahim Bidin et al., 1984; Lim, 1989; Chiew et al., 1989) and as boiler fuel (Rahim Bidin et al., 1984 and Azman Firdaus, 1988). Attempts to diversity the utilization of EFB have already been reported, e.g. for making tiles (Husin et al., 1985), to produce pulp and paper (Husin et al., 1989), and very recently for making glassy carbon (Mohamad Deraman, 1992).

The fibers or bundles of fibres in EFB are stringy and flexible in nature and they are physically stuck together to form vascular bundles. The average size of individual fibre is about 1 mm long, 25 microns wide and 3 microns thick (Husin et al., 1985). EFB contains about 77.7% holocellulose, made up of 44.2% α -cellulose, 33.5% hemicellulose and 20.4% lignin (Basiron and Husin, 1996). These components contribute to the carbon content of the EFB of 42%-43% (wet basis) (Gurmit et al., 1990).



Figure 1.1: Shredded Empty Fruit Bunch

Malaysia has a ready source of biomass in Empty fruit bunches (EFB) conveniently collected and available for exploitation in all palm oil mills. When convert the energy in the most efficient manner, Malaysia is well on the way to this most important sustainable source of energy for this century. The main achievement of using biomass-based Renewable Energy power generation is the reduction in greenhouse gas emissions (GHG).

In Sabah, large quantities of palm waste called Empty Fruit Bunches (EFB) are available from plantations where palm oil is produced. In its raw state, EFB is both very fibrous and wet. If it could be dried, it would be an excellent fuel for power boilers. FASC Malaysia has installed a KDS machine in the 14 MWe TSH Biomass Power Plants in Kunak, Malaysia, for the purpose of drying EFB. Called the KDS MF-777, it dries and shreds EFB so that it can be burned as a fuel. At present, only one-sixth of the fuel input needed by the TSH power plant is supplied by the KDS MF-777. The KDS MF-777 processes 3750 kg/hr of raw EFB having a moisture content of 52 % and produces 3000 kg/hr of shredded EFB which has a moisture content of 40 % - this is dry enough for burning on a grate. The power consumption of the MF-777 is only 200 kW, under these operating conditions. This translates to a drying energy consumption of only 960 kJ per kg of water removal (= 414 BTU/lb) or only 44 % of the latent heat of water, no other dryer technology can match the low energy consumption of the KDS MF-777. It is well-known among power plant engineers that every percentage point of moisture in the fuel causes 0.5-1 % reduction in the electricity produced. Thus, the estimated maximum possible increase in the TSH power plant output because of drying the fuel in the KDS MF-777 is 0.84-1.68 MWe. Thus, a net overall increase in the total power generated becomes possible due to the KDS MF-777.

Therefore, the cost of the KDS equipment can be recouped from the extra revenue from the increased electricity production. Oil palm empty fruit bunch (EFB) is yet to be fully utilized economically. EFB has been a subject of environmental concern, whereas its handling in the palm oil mill also consumes unproductive cost and energy. Since the supply of EFB is continuous at palm oil mills and annual production of EFB approximately amount to 8.5 million metric tons, this material is considered to have a great potential for commercial exploitation. Production of carbon products from EFB has been investigated since 2003 (Astimar et al., 2003). Recently MPOB has developed a process to prepare high porosity carbon and molecular sieve carbon (MSC) for gas filtration from EFB (Astimar et al., 2005a, b).

Porous carbon powder from EFB has to compete with carbon from petroleum extract and coal. With the recent rises in coal and petroleum prices, it is expected that the carbon powder from EFB can be competitive, besides offering other advantages by replacing raw materials from non-renewable sources (petroleum/coal extracts) with materials renewable materials (agricultural by-products), supports the policy of zero waste in the oil palm, industry and adding value to the oil palm EFB, and encouraging the utilization of renewable sources available as agricultural by-products for value added products.



Figure 1.2: Carbon Powder

There are many forms of carbon products in the market, for example, cokes, graphites, carbon and graphites fibers, carbon fibers-carbon matrix composites, adsorbent carbons and monoliths, glassy carbon, engineering carbons, carbon blacks, carbon films, diamond like films, carbynes, fullerenes, carbon nanoparticles, carbon nanotubes, carbon nanocones and multiwall carbon spheres.

Typical categories of precursor for Solid State Science and Technology, Vol. 13, No 1 & 2 (2005) 170-178 ISSN 0128-7389 171carbon product are hydrocarbons, petroleum, coal, polymer and biomass from palm oil industry such as oil palm stones and oil palm empty fruit bunches (EFB). Porous carbons such as activated carbons are particularly useful and commonly used owing to their large adsorption capacity, fast adsorption kinetics and relative ease of regeneration. They adsorb organic and other non-polar compounds from liquid and gaseous phases. In practice, activated carbon is found in two general forms: granular activated carbon (GAC) and powdered activated carbon (PAC). GAC by definition is composed of particles with sizes greater than 0.8 mm, whereas PAC is composed of particles smaller than that value. GAC is generally said to have a larger internal surface area and smaller internal pores, while PAC is thought to have larger pores and a smaller internal surface area.

The adsorption process has an edge over the other treatment methods due to its sludge free operation. Activated carbon is the most widely used adsorbent for this purpose. The wide usefulness of activated carbon is a result of its chemical and mechanical stability, high adsorption capacity and high degree of surface reactivity. Extensive studies have shown that activated carbon (AC) is efficient in the adsorption of numerous bio-resistant organic pollutants from an aqueous system. Activated carbon adsorption has been recommended by the *United States Environmental Protection Agency* (USEPA) as one of the best available technologies (BAT) in the removal of organic compounds. The major constraint of its usage in industrial applications is high production cost due to expensive materials used. Many investigators have studied the feasibility of less expensive materials of agricultural by-product resulting from the annual harvesting and industrial processing of various agricultural crops for production of activated carbon and its application in wastewater treatment.

The by-product has been shown to be potential materials in the production of activated carbon with efficient adsorptive capacity comparable with that of commercial activated carbon. There are two principal methods for making activated carbon, namely a high temperature oxidation with steam of a previously charred carbonaceous substance (coal, char and charcoal) and a lower temperature chemical dehydration or chemical reaction of a carbonaceous raw material. Inexpensive sources and cost-effective preparation methods are in demand because of the importance of adsorption in pollution control. Result from previous studies showed that Potassium hydroxide (KOH) treatment is able to increase the surface area and pore volume of the porous carbon pellet prepared from Self-Adhesive Carbon Grain (SACG). The porosity of this carbon pellet changed with the concentration of KOH. The mechanism of reaction between KOH and carbon samples can be found elsewhere. In this study, the porous carbon is prepared in pellet form. Different operating parameters including concentration and temperatures will investigate to evaluate quality of the advanced carbon material such as carbon electrode and molecular sieve carbon (MSC).

1.2 Problem Statement

The presence of huge productions of biomass (15m mt/yr) from palm oil plantation it's give an environmental problem to the palm oil mill site if the storage time is too long. Effective utilization of the EFB and other by- product is expected to resolve or at least to minimize this problem and then will help the mills to operate productively. Besides that, with low value of EFB compare with coal and petroleum prices, it is expected that the carbon powder from EFB can be competitive. Oil palm EFB having polymetric lignocelluloses component such as hemicelluloses and lignin, is a potential raw material for the preparation of advanced materials such as carbon electrode and molecular sieve carbon.

1.3 Research Objective

1. To prepare advanced carbon product from oil palm biomass such as carbon electrode and molecular sieve carbon.
2. To study the physical and mechanical characteristic of empty fruit bunch carbon electrode.
3. Preliminary study toward high porosity of Molecular Sieve Carbon (MSC) for gas filtration in the O₂ and N₂ separation.

1.4 Research Scope

To achieve the objectives of the research, the following scope of study are to be apply:

1. Effects concentration of H₂SO₄ treatment toward thermal characteristic of the EFB carbon precursors.
2. Effect concentration of H₂SO₄ treatment toward, density (ρ), young modulus (E), Rockwell hardness (H) and electrical conductivity (σ).
3. Effect of difference carbonization temperature on the BET analysis and high porosity carbon and molecular sieve (MSC) for gas filtration.

1.5 Rationale & Significance of study

1. Solve some of disposal problem.
2. Supports the policy of zero waste in the palm industry and adding value to the oil palm EFB.
3. Can be replacing raw material from non-renewable sources (petroleum/coal extracts) with material renewable materials (agricultural by product).
4. Increase the output of oil palm industry by turning a by-product into a resource for other related industry.
5. Increase value added product waste to wealth.

CHAPTER 2

LITERATURE REVIEW

2.1 Acid Activation

EFB has been found suitable for conversion (by pre-carbonization into self-adhesive carbon grains (SACG) that can be palletized without any binding agent (Deraman et al., 1998). A number of attempts have been made to improve thermal and chemical characteristic of the SACG produces from EFB (Deraman et al., 2000; Abdul Aziz et al., 2003).

The use of acids for the activation of the lignocellulosic materials to prepare high surface area porous carbon has been known (Mochida *et al.*, 1985; Guo & Lua, 1999; Guo *et al.*, 2005; Legrouri *et al.*, 2004). Basically, strong acids are an oxidation agent, which promotes the dehydration and redistribution of biopolymers in the lignocellulosic materials (Song and Lee, 1984). It involves in the cleavage of the ether bonds between the lignin and the cellulose, followed by recombination reactions in which larger structural units are formed, resulting a rigid cross linked solid (Helm and Young, 1989; Sabio *et al.*, 1995; El-Hendawy, 2003). Based on that hypothesis, using sulfuric acid (H_2SO_4) to treat towards the SACG of EFB will modify the thermal and chemical properties of SACG, hence would increase some of the physical and mechanical properties of the carbon pellets.

The qualities and characteristics of ACs depend not only on the physical and chemical properties of the initial material but also on the activation methods used. Generally, physical and chemical methods are used to prepare AC having high surface area. In the physical activation, a raw material is firstly carbonized and then activated by steam or carbon dioxide (CO_2). Lua and Yang carried out studies on the effect of physical activation on the characterization of AC prepared from pistachio-nut shells. In the chemical activation, a raw material is impregnated with an activating reagent and then heat-treated in inert atmosphere.

Chemical activation with zinc chloride ($ZnCl_2$) was studied by many researchers on different preparation conditions. However, Hourieh *et al.* studied the effect of $ZnCl_2$ concentration on the properties of AC using a raw material like pistachio-nut shell. Activation temperature, duration time in activating reagent solution, the amount and the type of activating reagent, activation time are important parameters that determine the quality of AC. The gas mixture was used as an inert atmosphere during activation as it is believed that CO_2 activation mainly causes the creation of microporosity while steam activation increases the development of mesoporosity to a higher extent.

Among the chemical activation methods the K_2CO_3 activation produced a very low yield of 19%, while the phosphoric acid activation at 500 °C resulted in a yield of 40%, which is significantly higher than the other activation methods and activating agents. For example, the annual output of rice husk (RH) worldwide and China is about 80 and 40 million tons respectively (Zhang et al., 2010). Chemical activation is a well-known method to obtain high-performance porous carbons. The most commonly used chemical activation agents are KOH, NaOH, H_3PO_4 and $ZnCl_2$ (Kubota et al., 2009), (Demiral and Gunduzoglu, 2010) and (Martin-Gullon et al., 2004). Alkali hydroxides are usually used to ◀prepare high surface area▶ and large pore volume porous carbons.

2.2 Porosity and surface area

According to the International Union of Pure and Applied Chemistry (IUPAC), the pores of a porous material are classified in three groups: micropores (width $d < 2$ nm), mesopores ($2 \text{ nm} < d < 50 \text{ nm}$) and macropores ($d > 50 \text{ nm}$) (Gregg & Singh 1982). Previous authors claimed that CO_2 activation of activated carbon was found could increase the micropore surface area of activated carbon, by partially oxidizing the tar, produces an opening of mesopores and macropores into micropores, and simultaneously followed by the widening of narrow miropores (RodriGuez-Reinoso *et al.*, 1995; Sanchez *et al.*, 2001; Rodriguez-Valero, 2000).

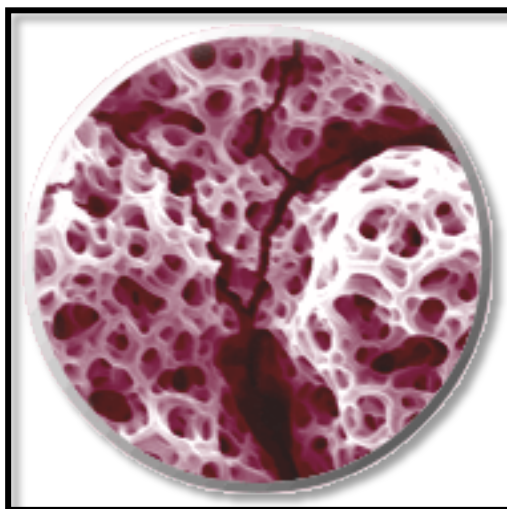


Figure 2.1: Porosity and surface area

Activated carbons, with their high porosity and large adsorption capacity, have been extensively used in various fields, such as industrial purification, chemical recovery operations, catalyst supports and electrode materials for batteries and electrochemical capacitors (Guo and Rockstraw, 2006). Wood, coal, petroleum have been used as carbon precursors (Amaya et al., 2007), (Karagoz et al., 2008) and (Mussatto et al., 2010). As is well-known, fossil fuels are finite, and lignocellulosic agricultural wastes are investigated as precursors vastly due to their renewability and huge amount.

In previous studies (Guo et al., 2003) and (Guo et al., 2002), good performance porous carbon ($3300 \text{ m}^2/\text{g}$, $1.88 \text{ cm}^3/\text{g}$) were prepared from RH by alkali hydroxide activation, but it was not economical and the activation agents could not be recovered easily in industry (Guo et al., 2002). From both economic and environmental perspectives, phosphoric acid is the preferred activation agent because the activation conditions are milder compared to alkali hydroxide, and it could be recovered in industry (Guastalli et al., 2009).

However, the surface area of porous carbons prepared from coal, wood and lignocellulosic materials by phosphoric acid activation is not large enough ($<2000 \text{ m}^2/\text{g}$). In this sense, there is great interest in using new precursors to prepare high-performance porous carbons by phosphoric acid activation. Surface area and porosity are important characteristics, capable of affecting the quality and utility of many materials. For this reason it is important to determine and control them accurately. Likewise, knowledge of porosity and surface area are frequently important keys in understanding the structure, formation and potential applications of different natural materials. Activated carbon (AC) is an adsorbent produced from a variety of carbonaceous source materials. Having high surface area and porosity, it is used as an adsorbent for removal of organic compounds from air and water streams. They are also used as catalysts and catalyst supports in the catalytic processes. Therefore, high surface area and porosity are very important for AC quality because the removal of large amounts of chemical compounds from gas or liquid streams on ACs. Adsorption via carbon is an expensive process. Therefore production of low cost AC has been developed. There are many studies on ACs done with a variety of shells and agricultural wastes. (K. Gergova, N. Petrov and S. Eser, 1994). The reason of choice of them for this aim is their abundance and availability.

Activated carbon with suitable pore structure having high surface area has good value realization, commercial acceptance and hence it is imperative to utilize processes that maximize the yield with good pore characteristics. Majority of the study reports only the pore structure and pore characteristics of the activated carbon, without the due mention to the yield of activated carbon. The yield as well as the pore structure of the activated carbon is widely reported to be influenced by the activation temperature, activation time and the impregnation ratio. Generally, the yield of activated carbon decreases with increasing activation temperature, activation time and impregnation ratio, while the pore characteristic improves with increase in the above stated parameters, mostly to an optimum value and decreases beyond. It can be observed that majority of the work reports only about the pore characteristics without mentioning the corresponding yield.

Among the reported literature the yield of activated carbon using physical activation methods is found to be less than 17 %, with the activation temperature around 900°C, while the combination of physical/chemical activation methods reports yield less than 30 % with the activation temperature around 800 °C, with an exception of ZnCl₂/CO₂ activation resulting in a yield of 37%. It can be observed that the yield of activated carbon varied widely depending upon the processing methods. Induced by the result due to Guo and Lua, and the advantages of phosphoric based activation methods due to Srinivasakannan and Bakar the present study attempts to explore further into the low temperature activation using phosphoric acid for the conversion of palm shells into activated carbon. Toward this experimental methods due to Srinivasakannan and Bakar is adopted, utilizing a two stage activation process in a self-generated atmosphere, at an activation temperature of 425 °C, with the activation time of 30 min, by varying the impregnation ratio of 0.5–3. The choice of low activation temperature and time is aimed at improving the process economics based on the recent report due to Gratiuto et al.

A carbon-rich solid product denoted as hydrochars was selected as a new carbon precursor, which was prepared from sulfuric acid hydrolysis solution of RH via dehydration and carbonization. Sulfuric acid is the suitable reagent for the high yield extraction of sugars from cellulosic based biomass, and it also performs well in carbonization of sugars (Harmer et al., 2009). The formation of the hydrochars containing large quantities of oxygen functional groups through the hydrothermal carbonization of sugars is the consequence of dehydration, polymerization and aromatization reactions (Wang et al., 2001). Combined with the characteristics of phosphoric acid activation, it is possible to prepare high surface area porous carbon using hydrochars as precursor.

Activated carbons are important materials, which have been widely used in various industrial applications. In general, carbon materials with the unique pore size distribution are due to the differences in precursors and treatments. In addition, activated carbons used in supercapacitors must have highly electrochemically accessible surface areas with mesoporous structures, which are the typical characteristics of wood-derived activated carbons. In laboratory, a series of studies were conducted to prepare porous carbons from various wood wastes and fruit shells by a physical activation method (steam), in which these carbons have been evaluated for the possibility of applications in industrial pollution control. Physical properties of the carbons including the BET surface area, pore size distribution, and the total pore volume were compared.

2.3 Separation process

Gas separation technology by adsorption process has been widely applied in petrochemicals, biochemical, environmental, oil and gas industries. One of the materials useful in such industries is molecular sieve carbon (MSC), which is a special class of activated carbon having discrete pore structure that allow it to discriminate between molecules on the basis of size. It can separate molecules based on rate of adsorption rather than on the differences in adsorption capacity. They are kinetic adsorbents that separate N_2 from air by faster sorption of O_2 (Hu & Vansant, 1995). The most important application of a Carbon Molecular Sieve (CMS) is the separation of nitrogen from air by pressure swing adsorption (PSA) technique (Foley, 1995).

Various types of MSC have been prepared from carbonaceous sources, such as coal (Miura & Hayashi, 1991), lignocellulosic material and biomass (Hu & Vansant, 1995; Nguyen and Do, 1995; Hayashi, 1999; Farris & Coe, 1992) and oil palm wastes (Guo & Lua, 1999; Tan & Ani, 2004). Generally, there are two major approaches in preparing the MSC, that are either based on controlled pyrolysis of carbon precursor or by modification of existing porosity of an activated carbon through carbon deposition technique.

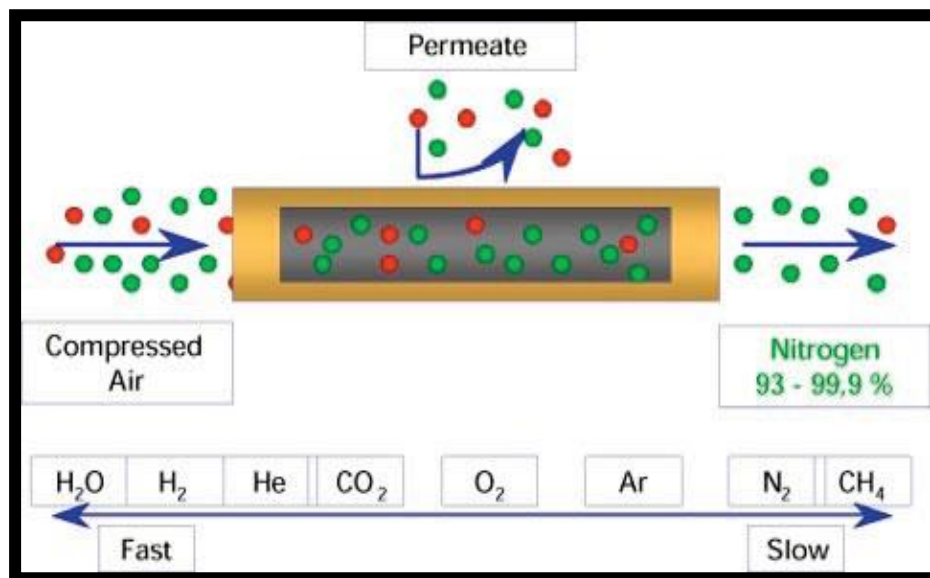


Figure 2.2: Process of separation of gases, (O_2/N_2)

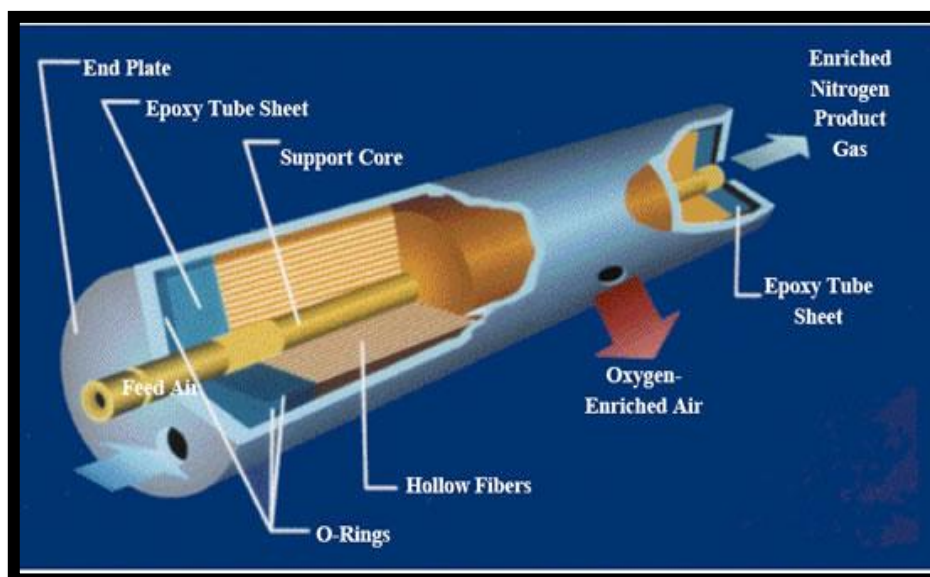


Figure 2.3: Separation of O_2 and N_2

Gas separation is an energy consuming process. In the industrial separation of gases, processes like distillation and pressure swing adsorption are commonly used. However, in the last decade polymeric membranes have been developed for large scale separation of gases and are presently applied as an alternative for the conventional processes. Carbon Molecular sieve (CMSs) have shown permeation and separation properties exceeding those of their polymeric precursor membranes. This has led to an extensive research into the field of CMS, with an emphasis on precursor material selection and pyrolysis trajectories (Joachim Petersen; Masaji Matsuda; and Kenji Haraya, 1997).

Many authors have reported on the preparation procedure of the polymeric precursor. This precursor can be either supported or an unsupported polymeric membrane. In the first case the polymeric membranes are supported by, e.g. flat or tubular configurations of porous inorganic materials, carbon or sintered stainless steel. The polymer can be applied to the support by ultrasonic deposition, dip coating, spin coating, and other comparable methods. Preparation of CMS membranes from porous precursors has been reported, but to obtain good separation values the precursor was coated before pyrolysis. We applied no coatings to our fibers before or after the pyrolysis. Strong adsorbate activated carbon and usually has an adsorption cross section s of 0.16 nm^2 for nitrogen adsorption at liquid nitrogen temperature, is revealed from experimental data to have a large surface area around $3000 \text{ m}^2 \text{ g}^{-1}$. Moreover, in the field of solid catalysis, the surface area of catalysts is an important factor in catalytic activity. Mesoporous silica and layer clay minerals have high surface areas of several hundred $\text{m}^2 \text{ g}^{-1}$ calculated by the BET method, indicating the possibility of application for efficient catalytic materials. Separation and purification of gaseous mixtures is an important unit in the chemical and petrochemical industries.

Nowadays, there is a growing demand for high purity products which boosts the importance of gas separation processes. Gas adsorption as a physical treatment technique is proved to be effective in processes which involve the gas separation and purification. Although adsorption may be a costly method however, utilizing low cost materials as adsorbent makes the adsorption process cost effective. Lignocelluloses biomasses are attractive materials as precursors for preparation of carbonaceous materials used in adsorption processes. Biomass is the only renewable source of carbon which can be converted to solid, liquid and gaseous product through various conversion processes. Currently, biomass provides about 14% of the world's energy consumption, but still large quantities of biomass have no specific use. They are burned in open air or dumped which generate pollutants including dust and acid rain gases such as sulfur dioxide and nitrogen oxides.

According to the growing trend towards the use of biomass-based energy and material in developed countries, it is important to utilize such potential wastes to produce energy or valuable commercial products. One of the promising technologies which utilize the wastes or plant matter involves the production of CMS from biomass-based materials. The basic structure of all lignocellulosic biomass comprises of three main natural polymers of cellulose $(C_6H_{10}O_5)_x$, hemicelluloses $(C_5H_8O_4)_m$ and lignin $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}]_n$. Lignin is a mononuclear aromatic polymer found in the cell wall of certain biomass, especially wood species, whose function is to cement cellulose fiber in plants.

It is the most abundant renewable carbon resource on earth after cellulose, with worldwide production of 40–50 million tons per year. Lignin is the most non-commercialized waste product which is proved to have considerable potential in the field of adsorption and preparation of activated carbon. In fact, lignin is rich in carbon and its molecular structure is similar to bituminous coal which makes it a suitable precursor for activated carbon production. Lignin which consists about 27% of the biomass content has low adsorption capacity in its natural form. But, its performance can be highly improved under appropriate conditions.

Generally, thermo-chemical processes such as pyrolysis are applied to generate char, oil or gaseous product from biomass. During thermal treatment, moisture and volatile compounds are removed from the biomass and solid chars are generated whose properties are different from the origin of the biomass materials. Such processes lead to materials with high porosity, large surface area and high pore volumes. Therefore, the generated char is an attractive and potential by-product for the preparation of activated carbon and carbon molecular sieve (CMS) and. CMS is an amorphous structure, carbonaceous material which is characterized by a very narrow micropore size distribution to discriminate molecules on the basis of their size and shape. It has practical use in the field of catalysis, membrane and separation of gaseous mixtures via pressure swing adsorption (PSA). The biomass-based CMSs have been extensively used for separation of nitrogen and oxygen from air stream and carbon dioxide and methane and, propane and propylene and benzene and cyclohexane from their mixtures.

Any carbonaceous material with low inorganic compounds can be used as a raw material for CMS preparation. But, use of lignocellulosic biomass as a cheap and abundant carbon source for generation of CMS will enhance the economical feasibility of the adsorption process. A survey of literature indicated that various lignocellulosic biomass have been used as the substrate for CMS production such as eucalyptus wood spruce, oak and beech wood some other resinous woods and, peach stone and, apricot stone, walnut shell and, macadamia nut shell, coconut shell and palm shell. Utilization of biomass for the production of porous carbons is well established industrially, as the demand is abundant due to varied industrial application. Activated carbons with highly developed surface area are widely used in a variety of industries for applications which include separation/purification of liquids and gases, removal of toxic substances, as catalysts and catalyst support. With the development of technology, the applications of activated carbons keep expanding, with newer application such as super-capacitors, electrodes, gas storage, and so on.

The importance of activated carbon as a popular adsorbent can also be realized from the quantum of the carbon related research which revolves around activated carbons. Activated carbons have been traditionally produced by the partial gasification of the char either with steam or CO₂ or a combination of both. Usually the physical activation is a two-step process which involves the carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, or their mixtures. The gasification reaction results in removal of carbon atoms and in the process simultaneously produce a wide range of pores (predominantly micropores), resulting in porous activated carbon. Physical activation process is widely adopted industrially for commercial production owing to the simplicity of process and the ability to produce activated carbons with well-developed microporosity and desirable physical characteristics such as the good physical strength.

In chemical activation process the precursors are impregnated with dehydrating chemicals such as H₃PO₄, ZnCl₂, K₂CO₃, NaOH or KOH and carbonized at desired conditions in a single step. Chemical activation offers several advantages which include single step activation, low activation temperatures, low activation time, higher yields and better porous structure. The chemical agents used are substances with dehydrogenation properties that inhibit the formation of tar and reduce the production of other volatile products. The disadvantage of chemical activation process is the need for an important washing step, which is time consuming due to number of washings required to completely remove the activation agent from the carbon. Of the several activating agents reported the most important and commonly used activating agents are phosphoric acid, zinc chloride and alkaline metal compounds. Phosphoric acid and zinc chloride are used for the activation of lignocellulosic material that have not been carbonized previously; whereas metal compounds such as KOH are commonly used for the activation of coal precursors or chars. As compared to zinc chloride the phosphoric acid is most preferred due to environmental problems associated with zinc chloride. Further activated carbons prepared using phosphoric acid has better acceptance in food, fine chemical and pharmaceutical applications due to its non-contaminating nature.

The rapid growth of Malaysia palm industries has ranked her the world's biggest exporter of quality palm oil with revenue of RM65 billion in years of 2008. For every 2.5 kg of crude palm oil produced, about 80 kg of palm shells are generated and thus are posing disposal issues. The global production of palm oil is reported to be around 48 million tons, which corresponds to a palm shell generation of 1500 million tons. The availability of palm shells, far exceed the total demand for activated carbon, which is estimated to be only around 1.2 million tons. The palm shell has no specific technical use and only a small portion is used as fuel to generate process steam in the palm-processing mill.

High density, relatively high carbon content and low ash content are desirable properties of a suitable precursor for the preparation of high-grade activated carbon. These renewable agricultural wastes are cost-effective alternatives to more expensive and polluting precursors like coal for the production of activated carbon. However, there has been little investigation work on the preparation of carbon adsorbent in a pellet form except from Inomate et al., (2002) that had prepared high porosity carbon pellets for methane transportation. It is thus the objective of this article to study the effects of H_2SO_4 treatment of EFB carbon precursor and different carbonization temperatures (600°C, 800°C and 1000°C) use to prepare the activated carbon on the physical and mechanical properties, as well as the pore structure of the carbon of the carbon pellets. Subsequently, an attempt will be made to increase the porosity of the carbon pellets by partial oxidation activation using CO_2 gas. It is anticipated that it would be possible to increase the BET surface area (S_{BET}), following which the O_2/N_2 separation capacity will be investigated.

CHAPTER 3

METHODOLOGY

3.1 Background

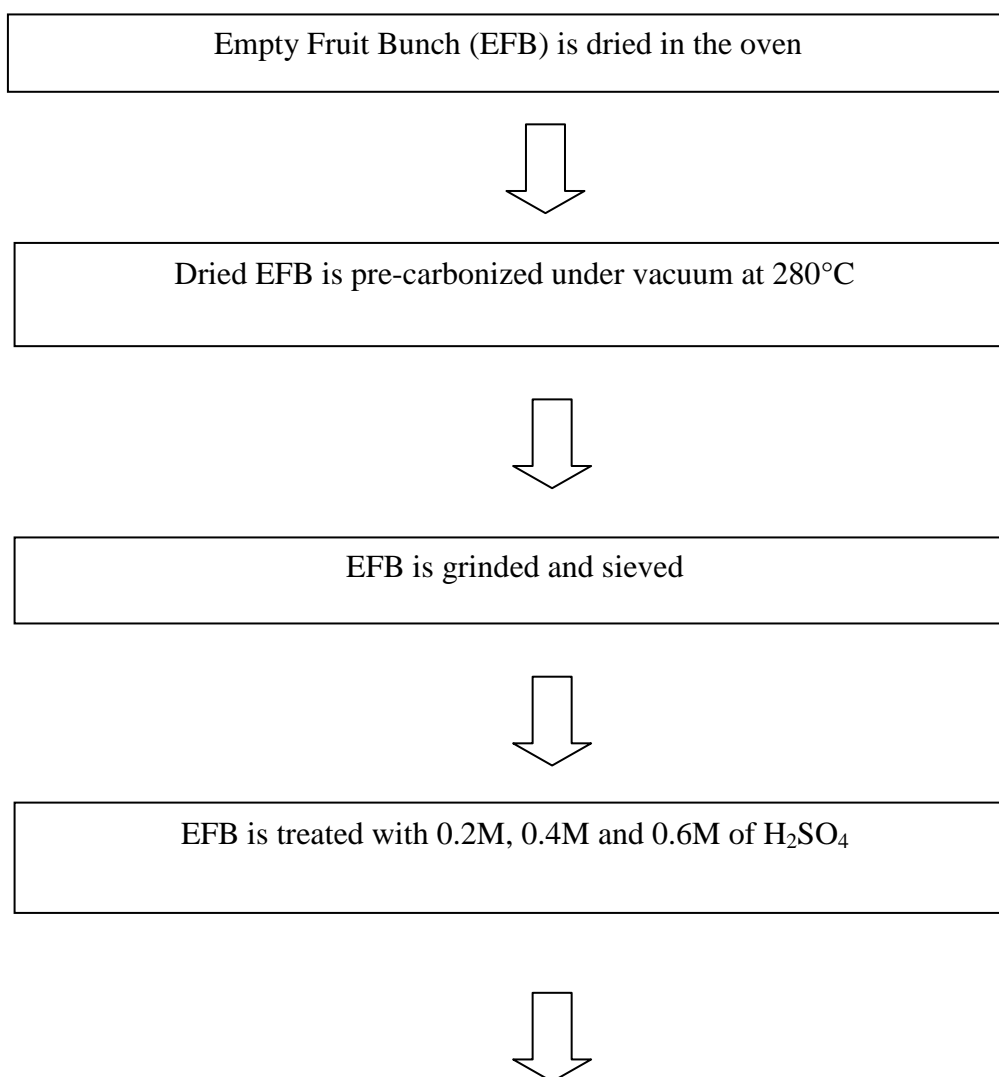
This chapter review the methodology used on this research where preparation of the sample carbon electrode, thermal characteristic and testing process. In this project, 3 samples of 3 different Molarities of carbon precursors at 0.2M, 0.4M, and 0.6M will be tested. The thermal characteristic and testing were conducted by using Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric Analysis. Figure 3.1 shows the overall general methodology for this experiment. Mechanical and physical characteristic such as density, electrical conductivity, hardness and young modulus also tested.

3.2 Material/Apparatus/Equipment

The chips from the dried oil palm Empty Fruit Bunch (EFB) are use in this study to produce carbon electrode and molecular sieve carbon. Empty fruit bunch that have been shredded was taken from LKKP corp.SDN.BHD.

3.3 Method/Procedure/Preparation

3.3.1 Flowchart of producing carbon electrode and molecular sieve carbon



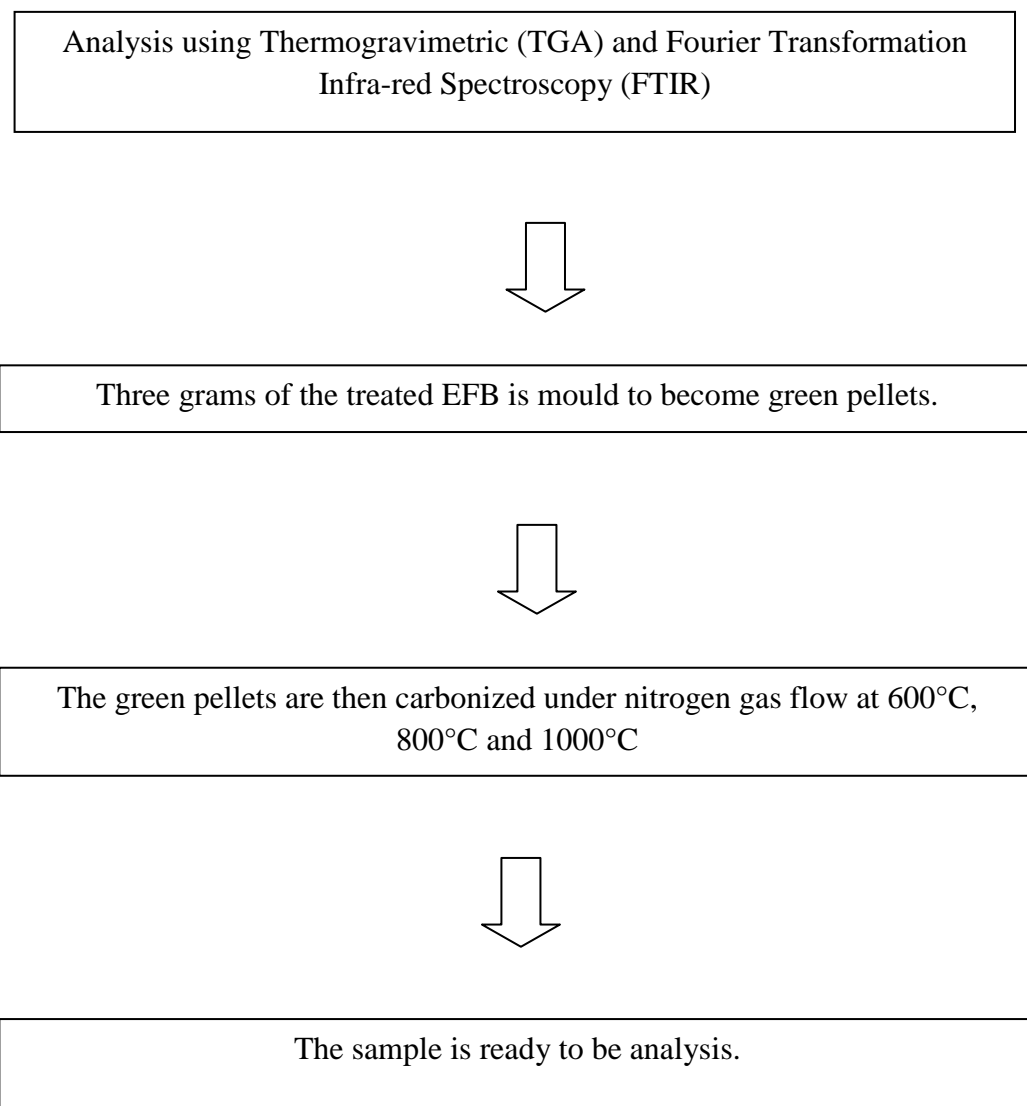


Figure 3.1: Flow chart of producing carbon electrode and molecular sieve carbon

3.3.2 Dried Empty Fruit Bunch



Figure 3.2: Dried Empty Fruit Bunch

Empty Fruit Bunch (EFB) is dried in the oven with temperature at 102°C to 105 °C for about 12 hour. It is to make sure all the water content in the empty fruit bunch is zero. It also to avoid from high vaporization occur during pyrolysis process.

3.3.3 Pre – Carbonization of Empty Fruit Bunch



Figure 3.3: Pre – Carbonization of Empty Fruit Bunch

Empty fruit bunches (EFB) that have been dried through pyrolysis process or pre – carbonization at 280 °C. The pre- carbonization process operates under vacuum where in vacuum pyrolysis, organic material is heated in a vacuum in order to decrease boiling point and avoid adverse chemical reactions. In this process not 100 percent of oxygen in the furnace can be removing, but in order to decrease the reaction in oxidation, the nitrogen was supply to the furnace.

3.3.5 Grinding and Sieving of Empty Fruit Bunch



Figure 3.4: Grinding and Sieving of Empty Fruit Bunch

(Carbon Pre-cursor)

The EFB carbon pre cursor that was prepared by pre-carbonization of the EFB chips follows by grinding and sieving through 150 micron sieve (Deraman et al. 1998). The EFB is grinded to reduce or to decrease the particle size of solid samples (homogeneity and ready to react with reagent).

3.3.6 Treated of Empty Fruit Bunch with Sulphuric Acid



a)



b)

Figure 3.5: a) Treated of Empty Fruit Bunch with Sulphuric acid

b) Treated carbon drying overnight at room temperature

The carbon precursor is then treating with 0.2M, 0.4M, and 0.6M of H_2SO_4 at $100^\circ C$ for 5 minutes before drying overnight at room temperature. Effect of the H_2SO_4 concentration toward the thermal characteristic of the carbon pre cursor will study by using Thermogravimetric analysis (TGA) and Fourier Transformation Infra-red Spectroscopy (FTIR) analysis.

3.3.7 Molding of the treated carbon.



Figure 3.7: Molding of the treated carbon

Three grams of treated carbon precursor is mould to produce carbon pellet.

3.3.8 Carbonization process



Figure 3.8: Carbonization process

The green pellets are then carbonized under nitrogen gas flow at 600, 800 and 1000°C in the High-Temperature Lift-Bottom Vacuum Furnace - Nabertherm. The temperature of the furnace will rise up to 280°C, at the rate of 1.0°C/ min and is left at that temperature for 60 minutes before finally raising it to 600°C at the rate of 3.0°C/min and then keep constant for 5 min before allowing it to cool down. For the carbonization at 800°C and 1000°C, the same heating profile was used which is increase to that temperature at 5°C/min and was keep at that temperature for another 5 minutes.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This section will review about the results from the tests that were made. The effect of the H_2SO_4 to the carbon precursor and effect of high temperature to the treated carbon will be discussed. The reasons for each result will be investigated and the data of each sample is plotted on the graph for better comparison and discussion. Besides characterization by FTIR and TGA, among the mechanical properties that were included in this section are electrical conductivity, hardness, flexural strength and Young's modulus. Besides that, physical characteristic such as bulk density and BET surface area are also will be review and discussed.

4.2 Nitrogen calculation

Nitrogen is inert gases, and because of the non-reactive properties of inert gases it's useful to prevent undesirable chemical reactions from taking place. A common techniques use of a high vacuum to remove air, and the use of an inert gas preferably argon, but often nitrogen. Nitrogen is used to supply to the furnace to release all the oxygen gasses in the furnace. So the flow rate of the nitrogen supply to the furnace need to known to make sure the gases of the nitrogen occupied with the total time of the experiment.



Figure 4.1: Nitrogen Gasses flow into the furnace

Volume of the nitrogen tank (full) = 7.1m^3

7.1m^3	1000L		60 min	= 38.89 L/h
	1m^3	10955 min	1h	

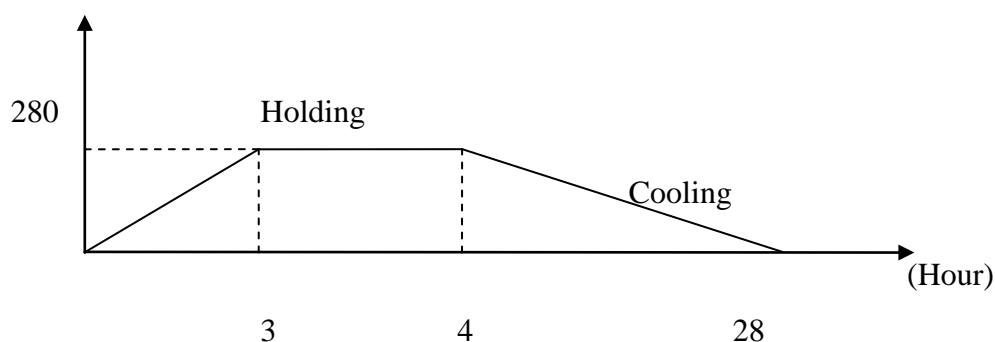
4.3 Pre- carbonization process

Pyrolysis is the thermal decomposition of biomass occurring in the absence of oxygen. Pyrolysis processes can be categorized as slow pyrolysis or fast pyrolysis. Fast pyrolysis is currently the most widely used pyrolysis system. Slow pyrolysis takes several hours to complete and results in biochar as the main product. In this experiment slow pyrolysis process has been used to pre-carbonize the empty fruit bunch (EFB). It is quiet difficult to control the temperature to make sure the empty fruit bunch do not completely burn in the furnace. If a complete combustion occurs in the furnace the EFB will change to the ash. EFB become to ash is the process that needs to be avoided. So, some heating profile was established to control the temperature of pre-carbonization of EFB.

4.3.1 Heating profile for pre- carbonization process

1st pyrolysis

Temperature (°C)

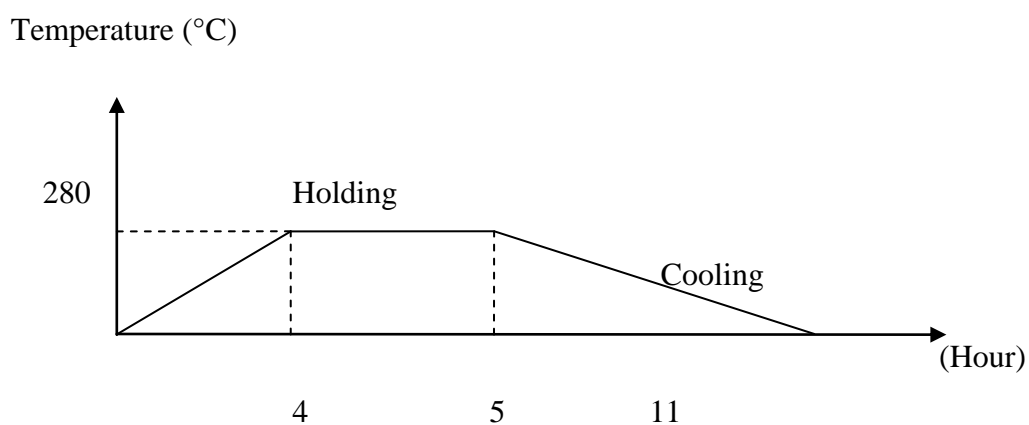


Pre-carbonization

No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
1	20	15.00	52.14	ok

Table 4.1: 1st pyrolysis

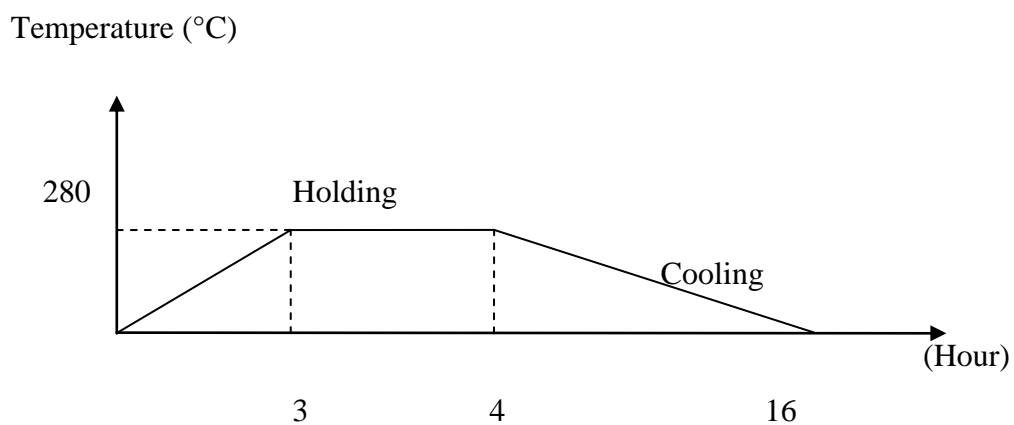
2nd pyrolysis



Pre-carbonization

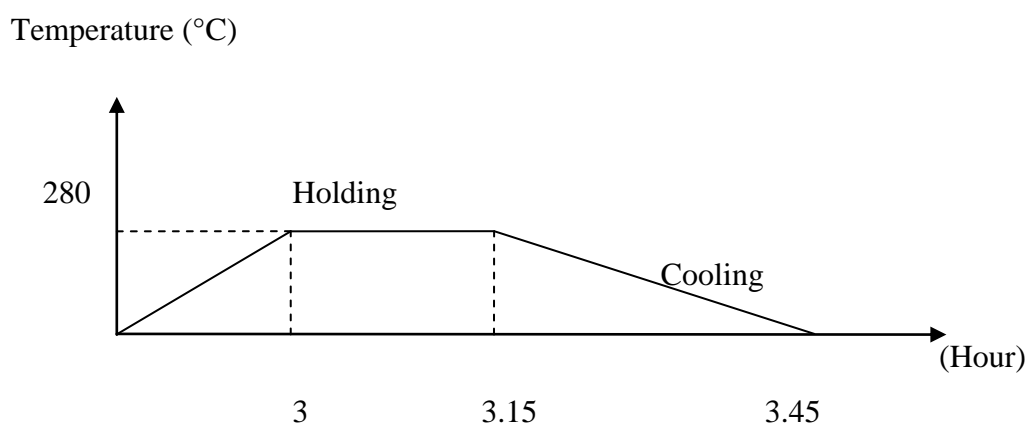
No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
2	52.06	27.36	47.46	EFB become ash

Table 4.2: 2nd pyrolysis

3rd pyrolysis

Pre-carbonization

No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
3	210.5	185.8	11.7	EFB become ash

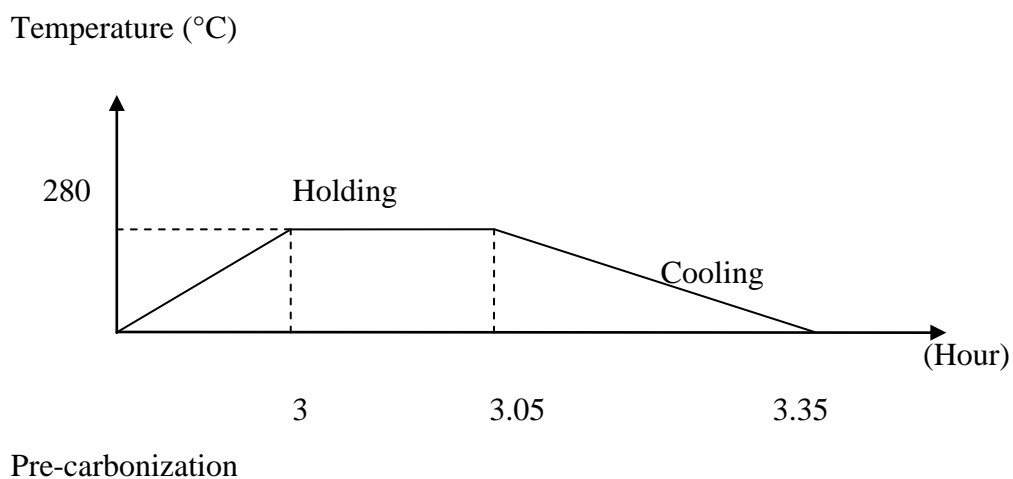
Table 4.3: 3rd pyrolysis**4th pyrolysis**

Pre-carbonization

No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
4	181.2	70.00	61.37	ok

Table 4.4: 4th pyrolysis

5th pyrolysis

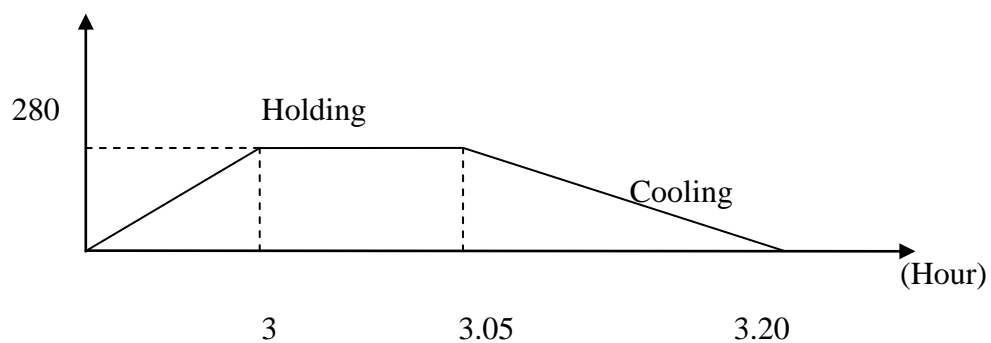


No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
5	176.3	95.00	46.11	ok

Table4.5: 5th pyrolysis

6th pyrolysis

Temperature (°C)



Pre-carbonization

No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
6	175.4	97.60	44.36	ok

Table4.6: 6th pyrolysis

4.3.1.1 Summary for the overall pyrolysis

No. of pyrolysis	Weight Before Pyrolysis (EFB) , g	Weight After pyrolysis (Carbon precursors) , g	Weight percent loss (%)	Result
1	20	15.00	52.14	ok
2	52.06	27.36	47.46	EFB become ash
3	210.5	185.8	11.7	EFB become ash
4	181.2	70.00	61.37	ok
5	176.3	95.00	46.11	EFB +ash
6	175.4	97.60	44.36	ok

Table 4.7: Summary for the overall pyrolysis

After pyrolysis process, the overall weight that has been calculated is about 200 g. Then, it is dividing to four difference concentration, which is 60 g for each molarity. The pyrolysis process the temperature at 200°C gives good results where the empty fruit bunch not change to ash. Actually, 280° C also can give a good result, but the holding time and the cooling time need to be control, means that the time that take to complete the process make it as minimum, not too long. From the observation, cooling time is one of the effects of pre-carbonization process. It is due to the absent of little amount of oxygen. Even the nitrogen gasses have been supply to the furnace, it still have a little amount of the oxygen because of furnace also expose to the air. So that, EFB need to take off from furnace after pyrolysis process to avoiding from complete.

4.4 Effect of H₂SO₄ concentration toward carbon precursor

Activation process is a process where sulphuric acid have been used as a activate agent to activated the carbon precursor. Sulphuric acid is used to activate this because H₂SO₄ have high concentration to break through the composition in the EFB like lignin and hemicelluloses. Carbon precursor was treated with sulphuric acid in different concentration. Sulphuric acid has been widely used to treat carbon precursor because it can form oxygen surface complex at the edge sites of carbon structure and hence affect the oxidation, structure, wetting adsorption, electrical and catalytic properties of carbon samples. Therefore, it was expected that carbon pellet prepared from the carbonization of green pellet from the acid sulphuric treated would be different from the untreated carbon pellet. Then the sample will be dried overnight. Then, the study of thermal characteristic had been analysis by FTIR and TGA.

4.4.1 Molarity of Sulphuric Acid

$$M = \frac{S.g \times \text{purity} (\%) \times 1000}{MW}$$

$$M = \begin{array}{|c|c|c|c|} \hline 1.84 \text{ g} & 0.96 & 1000\text{mL} & \text{mol} \\ \hline \text{mL} & & 1\text{L} & 98.08 \text{ g} \\ \hline \end{array}$$

$$M = 18 \text{ mol /L}$$

4.4.1.1 Dilution of Sulphuric Acid

0.2M

$$M_1V_1 = M_2V_2$$

$$V_1 = \frac{0.2 (500\text{mL})}{18}$$
$$= 5.56 \text{ mL}$$

0.4M

$$M_1V_1 = M_2V_2$$

$$V_1 = \frac{0.4 (500\text{mL})}{18}$$
$$= 11.11 \text{ mL}$$

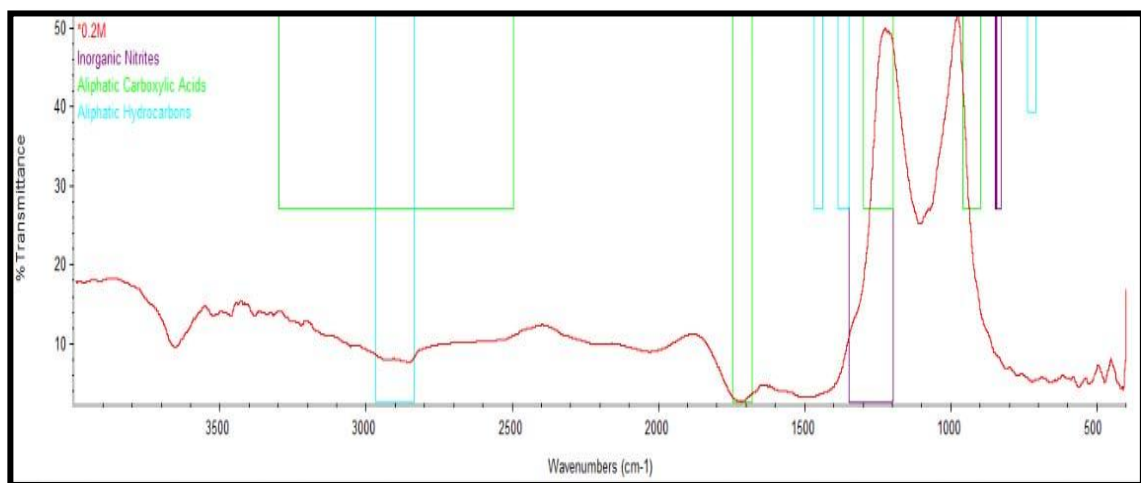
0.6M

$$M_1V_1 = M_2V_2$$

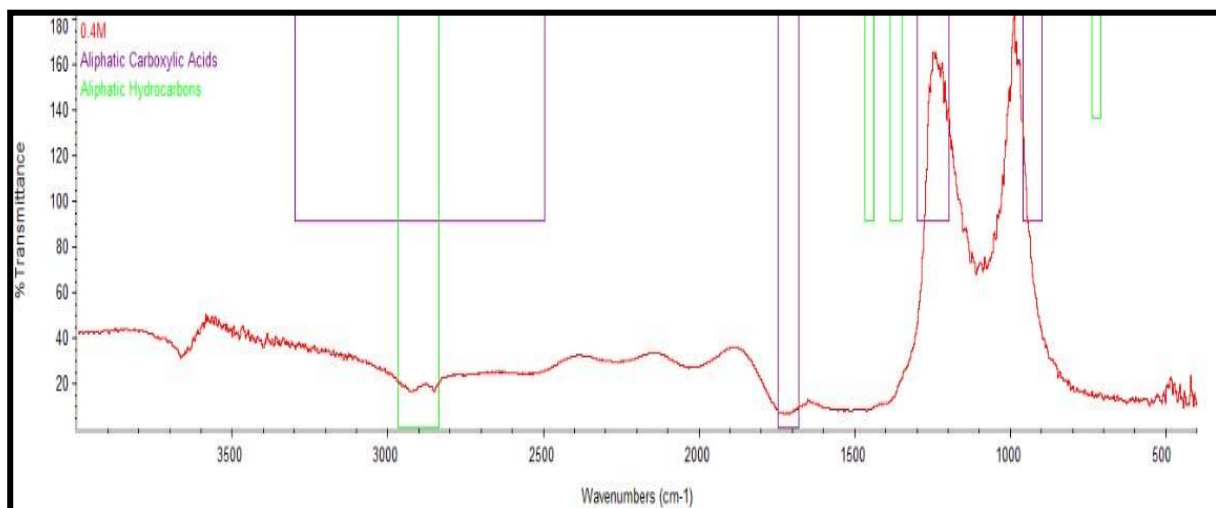
$$V_1 = \frac{0.6 (500\text{mL})}{18}$$
$$= 16.67 \text{ mL}$$

4.4.2 Characterizations using FTIR

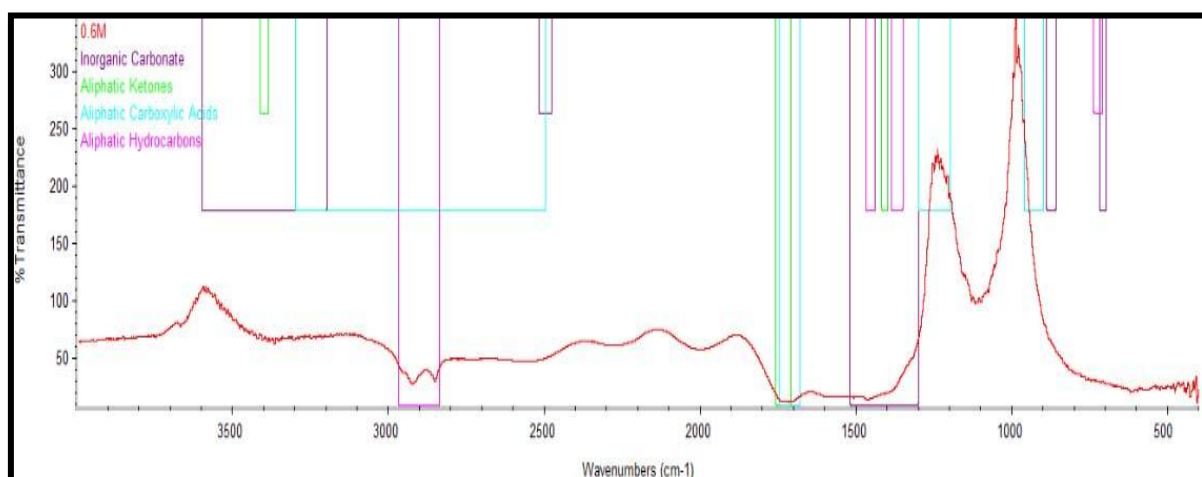
After treated carbon precursor with different concentration which is 0.2M, 0.4M, and 0.6 M, the FTIR analysis is carried out were used to detect functional groups and understand the structure of the carbon pre-cursor. The result depicted in Figure below.



Figures 4.2: FTIR analysis for 0.2M of sulphuric acid



Figures 4.3: FTIR analysis for 0.4M of sulphuric acid



Figures 4.4: FTIR analysis for 0.6M of sulphuric acid

From the observation in the graph above, FTIR analysis shows the carbon precursor slightly have same compound, which are in the 0.2M, the compounds are inorganic nitrite, aliphatic carboxylic acid, and aliphatic hydrocarbon. For 0.4M there are carboxylic acid, and aliphatic hydrocarbon in compound and in the sample that have treat with 0.6 M, there are four type of compound that can be measure, which are inorganic carbonate, aliphatic ketone, carboxylic acid, and aliphatic hydrocarbon.

Hydrocarbons which do not contain a benzene ring are called aliphatic hydrocarbons. Those which do contain benzene are called aromatic hydrocarbons. In aliphatic compounds, carbon atoms can be joined together in straight chains, branched chains, or non-aromatic rings (in which case they are called alicyclic). Aliphatic compounds can be saturated, joined by single bonds (alkanes), or unsaturated, with double bonds (alkenes) or triple bonds (alkynes). Most aliphatic compounds are flammable, allowing the use of hydrocarbons as fuel.

Carboxylic acids are organic acids characterized by the presence of at least one carboxyl group. The general formula of a carboxylic acid is R-COOH, where R is some monovalent functional group. A carboxyl group (or carboxy) is a functional group consisting of a carbonyl (RR'C=O) and a hydroxyl (R-O-H), which has the formula -C(=O)OH, usually written as -COOH or -CO₂H.

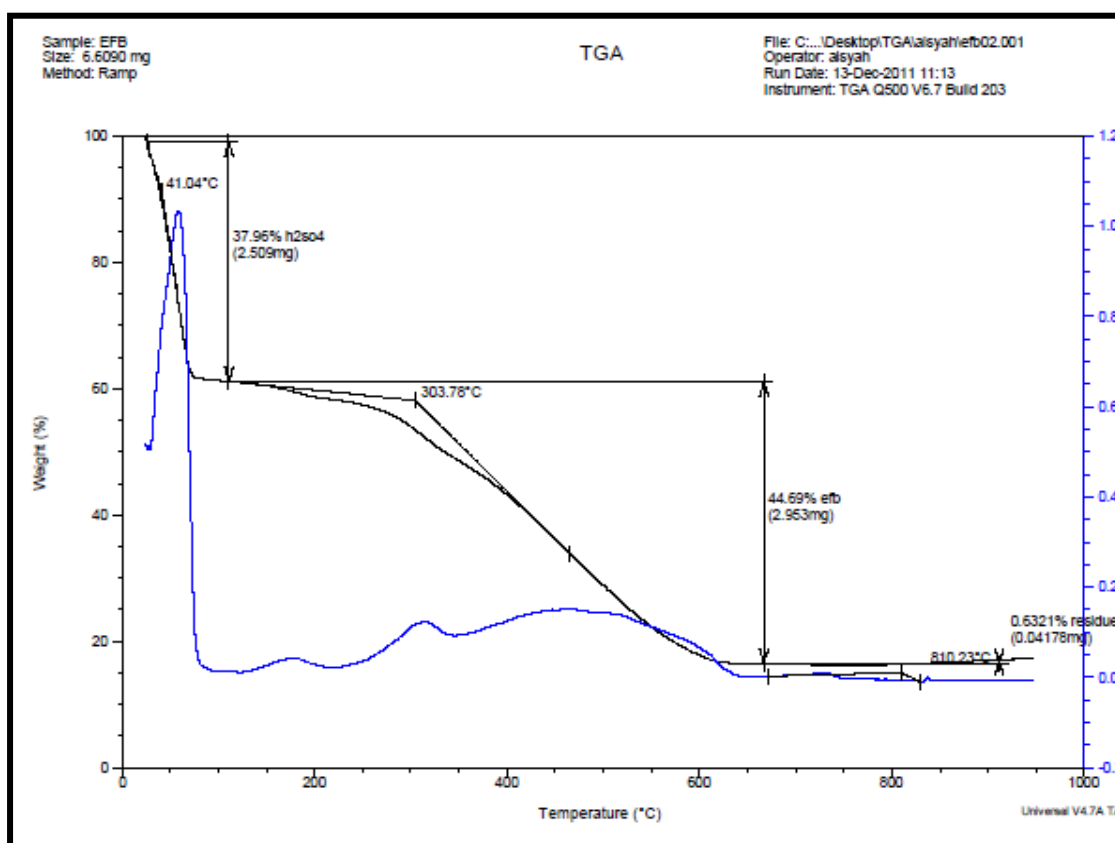
The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears at 1715 cm⁻¹. Conjugation of the carbonyl group with carbon-carbon double bonds or phenyl groups, as in alpha, beta-unsaturated aldehydes and benzaldehyde, shifts this band to lower wavenumbers, 1685-1666 cm⁻¹. The inorganic carbonates are salts of carbonic acid (H₂CO₃), containing the carbonate ion, CO₃²⁻, and ions of metals such as sodium or calcium. Inorganic carbonates comprise many and are the principal constituents of limestone and also comprise the hard parts of many marine invertebrates.

4.4.3 Characterization using TGA

TGA analysis was carried out to determine the thermal characteristic of the carbon precursor. The result was illustrated in the graph below.

Concentration (Molarity)	Weight after pyrolysis, (g)
0.2M	60
0.4M	60
0.6M	60

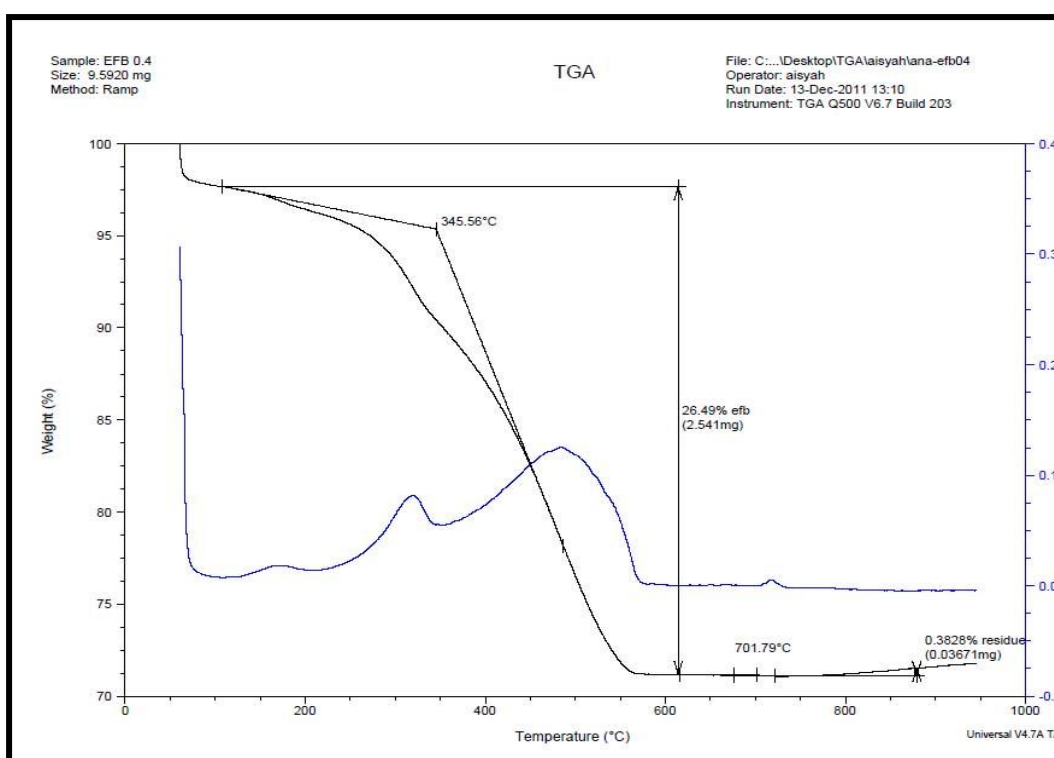
4.4.3.1 Carbon precursor treated with 0.2M of sulphuric acid



Figures 4.5: TGA analysis for 0.2M of sulphuric acid

The graph above shows the results of TGA analysis for carbon precursor treated with 0.2M. From the graph we can see that TGA was detecting some compound that burned at 41.04°C with 37.96% of weight percent. For the second peak, empty fruit bunch (EFB) was burned at 303.76°C and at 810.23°C the EFB become ash with 0.63% of weight percent.

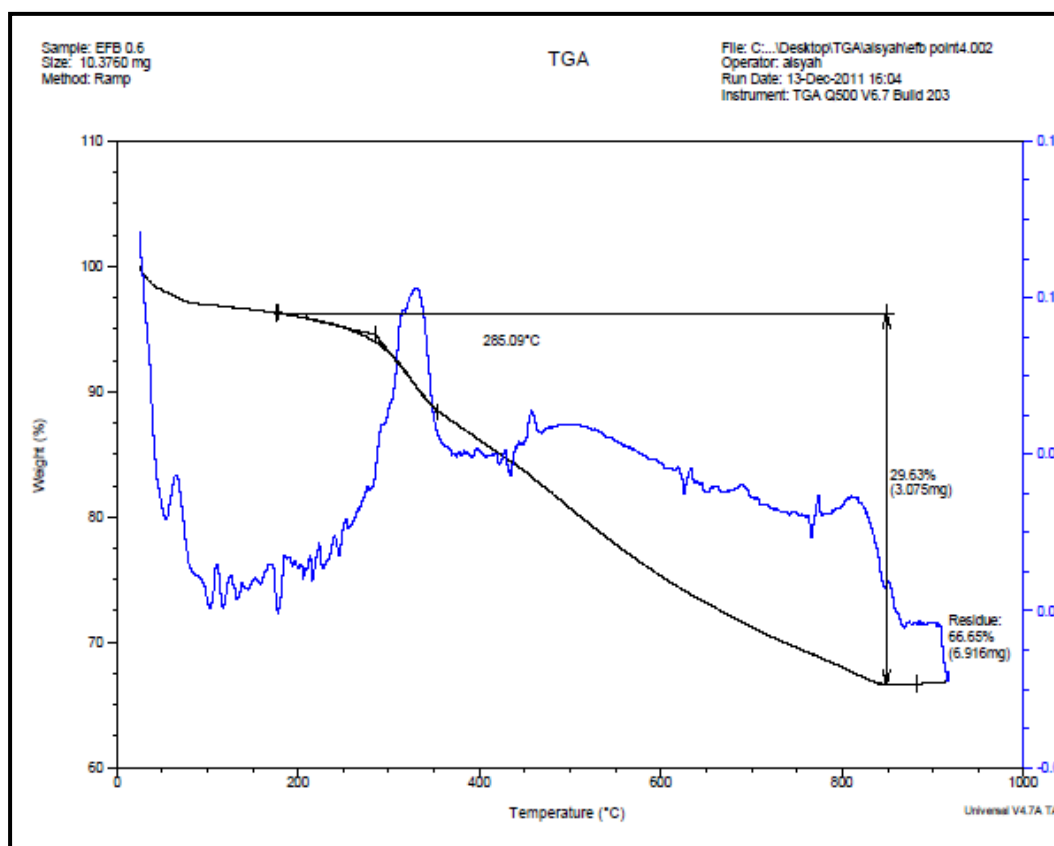
4.4.3.2 Carbon precursor treated with 0.4M of sulphuric acid



Figures 4.6: TGA analysis for 0.4M of sulphuric acid

The figure above shows a relationship between weight and temperature for 0.4 M. From the TGA analysis graph we can see that at the first peak, TGA was detecting empty fruit bunch burned at 345.56°C with 26.49% of weight percent. At 701.79°C the EFB become ash with 0.3828% of weight percent.

4.4.3.3 Carbon precursor treated with 0.6M of sulphuric acid



Figures 4.7: TGA analysis for 0.6M of sulphuric acid

The figure above shows the results of TGA analysis for 0.6 M which is graph of weight versus temperature. From the graph we can see that TGA was detecting empty fruit bunch burned at 285.09°C with 29.63% of weight percent. The EFB become ash with 0.63% of weight percent.

From the graph, we can discuss about increased the hygroscopic characteristic, hygroscopic is the ability of a substance to attract and hold water molecules from the surrounding environment of the treated EFB carbon pre - cursor as shown by the increase in the first peak rate of weight loss. The treatment with 0.6M of H₂SO₄ was broke down the lignocelluloses in the EFB carbon precursor and for 0.2 and 0.4 Molar of H₂SO₄ the lignocelluloses component still not decomposed on that temperature. Normally, the decomposition of cellulose and lignin occurs at about 300 °C (Bryne and Nagle 1997).

4.4.4 Physical properties

4.4.4.1 Calculation of bulk density of carbon pellet.

Sample	Before carbonization	After carbonization
0.0M	$V = \Pi j^2 T$ $= \Pi(1.504/2)^2(1.180) = 2.096 \text{ cm}^3$ $\rho = W/V$ $= 2.99/2.096 = 1.427 \text{ g/cm}^3$	$V = \Pi j^2 T$ $= \Pi(0.725/2)^2(1.076) = 0.444 \text{ cm}^3$ $\rho = W/V$ $= 1.63/0.444 = 3.67 \text{ g/cm}^3$
0.2M	$V = \Pi j^2 T$ $= \Pi(1.507/2)^2(1.174) = 2.094 \text{ cm}^3$ $\rho = W/V$ $= 3.00/2.094 = 1.433 \text{ g/cm}^3$	$V = \Pi j^2 T$ $= \Pi(0.760/2)^2(1.081) = 0.490 \text{ cm}^3$ $\rho = W/V$ $= 1.67/0.490 = 3.41 \text{ g/cm}^3$
0.4M	$V = \Pi j^2 T$ $= \Pi(1.507/2)^2(1.165) = 2.078 \text{ cm}^3$ $\rho = W/V$ $= 3.00/2.078 = 1.444 \text{ g/cm}^3$	$V = \Pi j^2 T$ $= \Pi(0.701/2)^2(1.073) = 0.414 \text{ cm}^3$ $\rho = W/V$ $= 1.64/0.414 = 3.96 \text{ g/cm}^3$
0.6M	$V = \Pi j^2 T$ $= \Pi(1.505/2)^2(1.180) = 2.096 \text{ cm}^3$ $\rho = W/V$ $= 3.01/2.096 = 1.455 \text{ g/cm}^3$	$V = \Pi j^2 T$ $= \Pi(0.692/2)^2(1.070) = 0.402 \text{ cm}^3$ $\rho = W/V$ $= 1.63/0.402 = 4.05 \text{ g/cm}^3$

Table 4.8: Density of the sample before and after carbonization

Sample	Before carbonization				After carbonization			
	W (g)	T (mm)	D(mm)	$\rho(\text{g/cm}^3)$	W (g)	T (mm)	D (mm)	$\rho(\text{g/cm}^3)$
0.0M	2.99	11.80	15.04	1.427	1.63	10.76	7.25	3.67
0.2M	3.00	11.74	15.07	1.433	1.67	10.81	7.60	3.41
0.4M	3.00	11.65	15.07	1.444	1.63	10.73	7.01	3.96
0.6M	3.01	11.63	15.05	1.455	1.60	10.70	6.92	4.05

Table 4.9: Weight (W), Thickness (T), Diameter (D), density (ρ) of the untreated sample (0M), treated sample (0.2M, 0.4M, 0.6M).

4.4.4.2 Before Carbonization

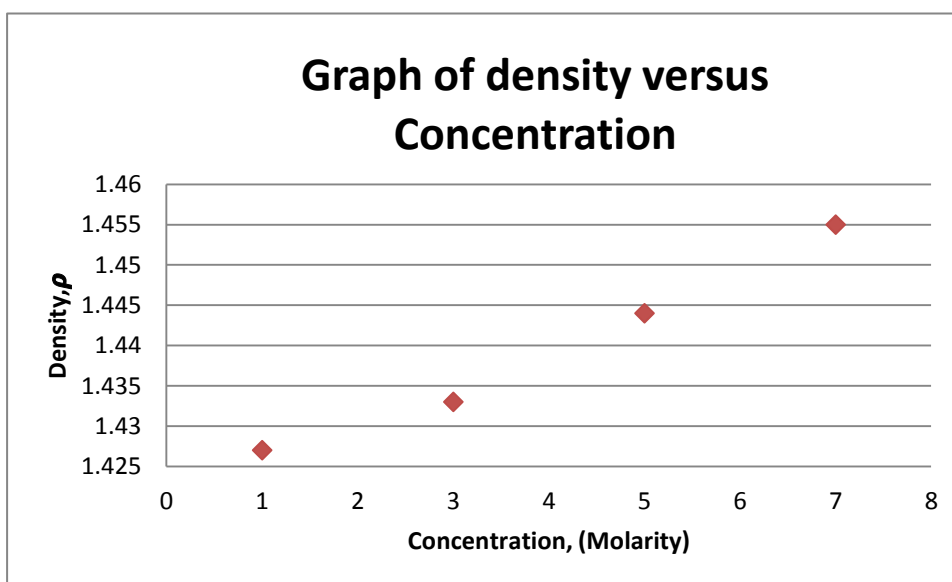


Figure 4.8: Graph of Density versus Concentration for before carbonization

4.4.4.3 After Carbonization

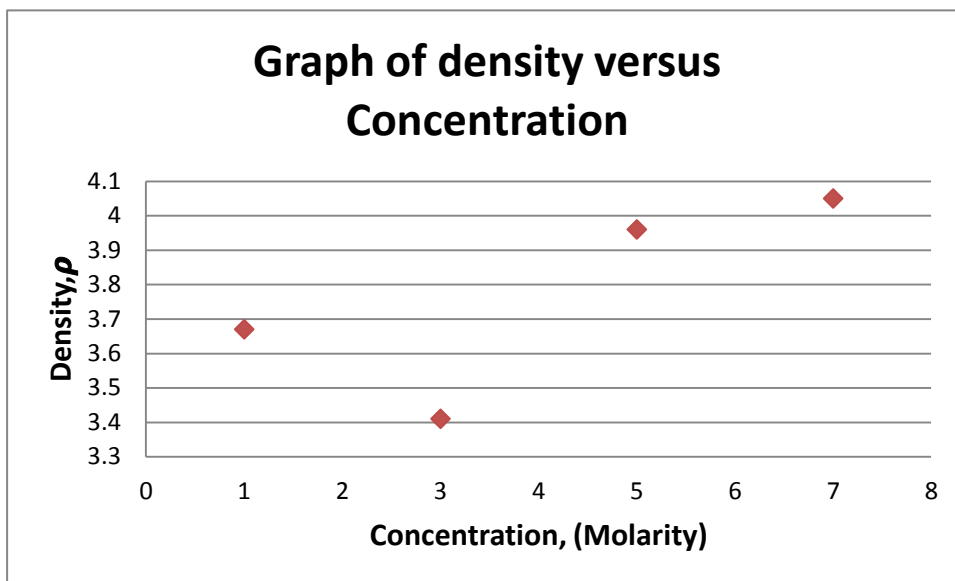


Figure 4.9: Graph of Density versus Concentration for after carbonization

From data in table 4.9 and figure above, the result shows that the value of density is increased when green pellet was treating with different concentration of acid sulphuric. This is because property of carbon precursor is heavier in weight after chemisorp oxygen from sulphuric acid. Besides that, table 4.9 also show that after carbonization the density of carbon pellets treated with 0.2M, 0.4M and 0.6M are slightly higher compare to the sample untreated sample. This may be due to less porosity development which occurred in sample 0.2M, 0.4M and 0.6M during carbonization because acid has dissolved some of the volatile matters in the green pellets.

The role of lignin in EFB fibres is to bind the cellulose and hemicellulose to form a composite structure. Hemicelluloses have partially decomposed due to pre-carbonization and lignin is no longer functioning as a cementing agent. The collapse of the composite structure makes the pre-carbonized EFB fibre brittle and therefore can be easily grinded into powder from carbon precursor. Therefore, it is possible that an increase in acid concentration can expedite the breaking of the pre carbonized EFB fibres into smaller particle size during grinding process. Green pellets from carbon powder a smaller particle size allow the formation of a stronger inter-particles bonding during carbonization and hence result in a stronger and better microstructure of carbon pellet after carbonization.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The research shows the potential for producing advanced carbon products from oil palm biomass such as carbon electrodes and molecular sieve carbon has been very encouraging. The analysis had shown the effect of concentration and temperature to the carbon precursor and carbon pellet in the production of advanced carbon materials. Thus, several conclusions that can be outline:

- 1 Air mixing and high temperature expose to the carbon pellet during carbonization process was affected the properties of carbon pellet, thus advanced carbon product such as carbon electrode and molecular sieve carbon can't be prepared.

- 2 The physical characteristic increase proportionally to the concentration of acid sulphuric, which is carbon pellet treated with 0.6M of H_2SO_4 give highest density.
- 3 High temperature gives high porosity of Molecular Sieve Carbon (MSC) for gas filtration in the O_2 and N_2 separation.

5.2 Recommendation

From the experimental work, several important recommendations should be carried out in such as:

- i. The raw material which is soft empty fruit bunch (EFB) need to mix with another hard palm shell to ensure the good and strong binding.
- ii. More innovative experimental works needed to solve current problematic methodology
- iii. More control of key parameters such as temperature and time during slow pyrolysis or pre- carbonized and carbonization.
- iv. Need to optimization of grinding time to get the right particle size of the carbon precursor.
- v. An innovative process of slow pyrolysis of the EFB chips has been able to produce carbon precursor and further H_2SO_4 treatment has enhanced the cross linking process during the carbonization of the carbon pellet.

REFERENCES

- ASTIMAR A A; MOHD B W; LIM W S (2007).Advanced carbon products from oil palm biomass, *Journal of Proceedings of The PIPOC 2007 International Palm Oil Congress (chemistry & Technology)*.
- ASTIMAR A A; MOHAMAD D; ROPANDI M; ANIS M; WAN HASAMUDIN; RIDZUAN R; ISMADI I (2006). High porosity carbon powder from oil palm empty fruit bunches for adsorbent products, *Article of MPOB*, p.1511-7871.
- ASTIMAR A A; MOHD B W; CHOO Y M (2008).Advanced carbon products from oil palm biomass, *Journal of Oil palm Research*, p.22-32.
- ASTIMAR A A; MOHAMAD D; ROPANDI M; ANIS M; WAN HASAMUDIN W H; RIDZUAN R; ISMADI I (2006). Carbon black from empty fruit bunch, *Article of MPOB*, p.336.
- ASTIMAR A A; WAN HASAMUDIN W H; ZAWAWI I; ROSNAH M S; ROPANDI M; ANIS M (2009). A Pyro-ligno binder from oil palm empty fruit bunch, *Article of MPOB*, p.467.
- ASTIMAR A A; MOHAMAD D; ROPANDI M; ANIS M; WAN HASAMUDIN W H; RIDZUAN R; ISMADI I (2006). Electrical carbon brushes from oil palm empty fruit bunches, *Article of MPOB*, p.339.
- IZAN R M; MOHAMAD, D (2004).Nitric acid treatment of empty fruit bunch (EFB)- Effect the microstructure and mechanical properties of the product, *Journal of Solid State Science &Technology* , 12(1):185-191.
- MOHAMAD, D; RAMLI, O (1995).Thermal conductivity of pellets prepared from oil palm bunches, *Journal of Pertanika J Science &Technology*,5(1):15-24.

- MOHAMAD, D (2006). Carbon pellets prepared from fibres of oil palm empty fruit bunches: A Qualitative X-ray Diffraction Analysis, *Journal of Porim Bulletin* 26.
- MOHAMAD, D; RAMLI O; S.ZAKARIA; I.R. MUSTAPA; M. TALIB; N. ALIAS; R. JAAFAR (2002). Electrical and mechanical properties of carbon pellets from acid (HNO₃) treated self – adhesive carbon grain from oil palm empty fruit bunch, *Journal of Material science*, 37:3329-3335.
- ROPANDI M (1995). Activated carbon production from oil palm waste and by-product-pilot plant study, *Article of PORIM*, p.44.

APPENDIX A

Gantt chart / Project Schedule PSM I

ACTIVITY	JANUARY				FEBRUARY				MARCH				APRIL				MAY			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Topic selected		■																		
Meeting with supervisor		■	■	■	■	■	■	■	■	■	■	■	■							
Finding journal and information			■	■	■	■														
Visit Palm Oil Mill Factory, LCSB Lepar.						■														
Attend a Research Methodology Seminar : How to write a good						■														
Writing proposal (draft)						■	■	■												
MPOB visited								■												
Order chemical									■	■										
Prepare slide presentation									■	■	■									
Presentation											■									
Finalize proposal report												■								
Submit report proposal													■							

Gantt chart / Project Schedule PSM II

ACTIVITY	SEPTEMBER				OKTOBER				NOVEMBER				DISEMBER				JANUARY			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Detailed research on methodology		■	■	■																
Start the experiment					■	■	■	■	■	■	■	■	■							
Data analysis and thesis writing														■	■	■	■			
Correction and preparation of thesis writing															■	■	■			
Prepare slide presentation																	■			
Final presentation																		■		
Compile and submit the report																			■	