STUDY ON THERMAL DECOMPOSITION AND CHARACTERIZATION OF PALM OIL WASTE AND FORESTRY RESIDUES

SITI NOR FADHILAH BT YASIM

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

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JULY 2015

ABSTRACT

Currently, researchers try to find another alternative energy sources to reduce dependence on fossil fuels, and also to fill the gap left through depletion of oil, gas and coal after 2088 and onwards. Malaysia is a second largest palm oil producer with total of 5.33 million hectares palm oil plantation. Production of palm oil in year 2013 increases to 19.22 million tonne from 18.79 million tonne in year 2012. Meanwhile in year 2014, production predicted is more than 19.55 million tonne. From the increasing of palm oil production, it shows that production of palm oil waste (biomass) also increases. Due to the huge amount of biomass generated yearly, Malaysia has a potential to utilize the biomass efficiently and effectively as an alternative energy source to replace fossil fuels. However, biomass has several problems such as high moisture content, low calorific value, and low density as compared to fossil fuels, therefore pretreatment of biomass is required. In this study, torrefaction was used as a pretreatment method for biomass. Torrefaction is strongly depended on the thermal decomposition behavior and composition of lignocellulosic constituents, and thermal decomposition profile was studied by using thermogravimetric analyzer (TGA). In this study, all the material were dried at 105 ºC with moisture content left is less than 10%. After that, decomposition profile/region was monitored by using TGA Q500 with different heating rate which is 10 ºC/min and 20 ºC/min, initial temperature set at 30 ºC and final temperature at 600 ºC. Flow rate of nitrogen gas at 100 ml/min was used. In this work, four samples were used, which are empty fruit bunch (EFB), palm kernel shell (PKS), mersawa and durian. Decomposition region of biomass start with hemicellulose, followed by cellulose and then lignin being last to decompose. From TGA graph, below 100 ºC, biomass loss their weight 5 – 10% due to water evaporation. From 100 – 500 ºC, the weight loss about 70 – 80% was due to high volatile matter. Then, temperature above 600 ºC weight loss found to be 10 – 20%. Study also revealed that the rate of decomposition EFB is faster than PKS due to high content of hemicellulose. Mass composition of lignocellulosic in biomass affects the rate of decomposition because the hemicelluose can enhance the decomposition rate and the lignin can reduce the decomposition rate of biomass. This TGA analysis is useful to design the torrefaction (mild pyrolysis), pyrolysis and gasification unit according to biomass thermal stability. In order to differentiate, investigate, or comparing decomposition characteristic between biomass, more biomass sample can be tested (other type of biomass) to see the trend of torrefaction process.

ABSTRAK

Ketika ini pengkaji cuba mencari sumber tenaga alternatif untuk mengurangkan kebergantungan terhadap bahan api fosil, dan juga sebagai tenaga baru untuk masa hadapan pada tahun 2088, yang dijangka akan kehabisan tenaga iaitu dari minyak, gas, dan arang batu. Malaysia merupakan negara kedua terbesar dalam penghasilan minyak kelapa sawit dengan mempunyai sebanyak 5.33 juta hektar ladang kelapa sawit. Penghasilan kelapa sawit pada tahun 2013 meningkat 19.22 juta tan dari 18.70 juta tan pada tahun 2012. Manakala pada akhir tahun 2014, penghasilan dijangka meningkat lebih daripada 19.55 juta tan. Daripada peningkatan hasil kelapa sawit tersebut, ia menunjukkan pengeluaran sisa kelapa sawit (biojisim) juga meningkat. Oleh sebab jumlah biojisim yang terhasil setiap tahun adalah besar, Malaysia mempunyai kelebihan untuk menggunakan biojisim sebagai sumber tenaga alternatif untuk menggantikan bahan api fosil. Tetapi biojisim mempunyai beberapa masalah seperti tahap kelembapan yang tinggi, rendah nilai kalori, dan ketumpatan yang rendah dibandingkan dengan bahan api fosil. Oleh sebab itu, biojisim memerlukan pra rawatan. Dalam kajian ini, *torrefaction* akan digunakan sebagai pra rawatan biojisim. *Torrefaction* bergantung kepada penguraian terma dan komposisi komponen *lignocellulosic,* dan profil penguraian terma telah di analis menggunakan *thermogravimteric analyser* (TGA). Dalam kajian ini semua bahan dikeringkan pada suhu 105 ºC dengan kelembapan sebanyak kurang daripada 10%. Selepas itu, profil atau kawasan penguraian diperhatikan menggunakan TQA Q500 dengan nilai kadar pemanasan yang berbeza iaitu 10 ºC/min dan 20 ºC/min, suhu awal di tetapkan pada 30 ºC dan suhu akhir pada 600 ºC. Kadar aliran gas nitrogen sebanyak 100 ml/min digunakan. Dalam kajian ini, empat bahan ujian digunakan seperti *empty fruit bunch* (*EFB*), *palm kernel shell* (*PKS*), mersawa and durian. Penguraian biojisim bermula dengan *hemicellulose,* diikuti oleh *cellulose* dan yang terakhir adalah *lignin.* Berdasarkan graf TGA, suhu dibawah 100 ºC, berat biojisim 5 – 10% hilang disebabkan oleh pengewapan air. Suhu dari 100 – 500 ºC, 70 – 80% berat biojisim hilang disebabkan mengandungi peruapan bahan yang sangat tinggi. Kemudian, suhu di atas 600 ºC berat hilang ialah diantara 10 – 20%. Kajian mendapati kadar penguraian *EFB* lebih cepat berbanding *PKS* yang disebabkan oleh kandungan *hemicellulose* yang tinggi. Komposisi berat *lignocellulosic* dalam biojisim menjejaskan kadar penguraian kerana *hemicellulose* boleh mempercepatkan kadar penguraian dan komposisi *lignin* boleh mengurangkan kadar penguraian biojisim. Analisa TGA ini sangat berguna untuk medapatkan unit gasifikasi, pirolisis, and separa pirolisis. Dicadangkan, untuk membezakan, mengkaji, atau untuk perbandingan karakter penguraian antara biojisim, penambahan biojisim boleh diuji (biojisim yang berbeza) untuk melihat aliran proses *torrefaction.*

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

Biogen	Biomass-based power generation and co-generation
EFB	Empty fruit bunch
FFB	Fresh fruit bunch
GEF	Global environment facility
KeTTHA	Kementerian Tenaga Teknologi Hijau dan Air
LCSB	LKPP corporation Sdn Bhd
LKPP	Lembaga Kemajuan Perusahaan Pertanian
MPOB	Malaysian palm oil board
OPP3	Third outline perspective plan
PKS	Palm kernel shell
PMF	Palm mesocarp fibre
PKC	Palm kernel cake
POME	Palm oil mill effluent
RE	Renewable Energy
SPSSB	Seng Peng Sawmill Sdn Bhd
TGA	Thermogravimetric analyzer
9MP	Ninth Malaysia Plan

1 INTRODUCTION

1.1 Background

In 2088, the world expected to run out of fossil fuels. Fossil fuels are known as hydrocarbons, primarily coal, oil, and natural gas formed from the remains of dead plants and animals. Typically, millions of years are needed to get the fossil fuels. Meanwhile, currently over 11 billion tonnes of oil in fossil fuels was consumed every year and crude oil are vanishing at rate of 4 billion tonnes per year, with this rate of consumption, this oil deposits will be gone by the year 2052. Although natural gas will be reserved to fill the energy gap left by oil, it will only sustained until the year 2060 and with the energy reserved from coal, it will be enough until year of 2088 (Gore, 2014).

Currently, researchers try to find another alternative energy sources to reduce dependence on fossil fuels, and also to fill the gap left through depletion of oil, gas and coal after 2088 and onwards. Last two decades, researchers found that the biomass can be used as source of renewable energy. Biomass is 3rd largest primary energy source after coal and oil (Linghong *et al*., 2010). The reason why biomass as a renewable source of energy is because, the energy is released in the form of heat during the combustion and biomass is a renewable energy source of carbon which is can be converted into convenient solid, liquid and gaseous fuels through different conversion process (Ahmed *et al.*, 2011).

Energy conversion from biomass can be done by using different process which are thermochemical (e.g. combustion, and gasification), biological (e.g. anaerobic digestion and fermentation), and chemical process (e.g. esterification). However, raw biomass cannot be converted directly because, it have several problems due to its characteristics, and pretreatment of biomass needed. There are several method for a pretreatment of biomass which are pyrolysis, torrefaction (mild pyrolysis), and microbioal pretreatment. From this three methods, torrefaction is the most suitable, and it is strongly depended on thermal decomposition behavior and lignocellulosic component (Suzana *et al.*, 2011).

1.2 Motivation

Biomass is a 3rd largest primary energy source after coal and oil. Percentage of energy provided from oil is 40%, from coal is about 28%, from biomass is about 20%, and from natural gas which is 12% (Energy resources, 2014). Malaysia is one of the countries with the largest palm oil producer in the world, which is more than 7 million tonnes of empty fruit bunch (EFB), 4.5 million tonnes of palm mesocarp fiber (PMF), and 1.9 million tonnes of palm kernel shell (PKS) are generated as solid wastes (biomass) with increasing of 5% annually (Yang *et al.*, 2004). Total production of palm oil in the end of 2014 is predicted to be more than 19.55 million tonne, and every 20,000 tonnes of fruit fresh bunch (FFB) were collected, about 4,600 tonnes EFB are produced. Increasing in palm oil production, cause the solid wastes increase, in Malaysia, there are about 200 palm oil mills in total operations.

Meanwhile forestry residues is a biomass material that remained in forest and has been harvested for timber, including logging residues, excess small pole trees, natural attrition, extracting stem-wood for pulp and a rough or rotten dead wood (EPA, 2014). Due to the huge amount of biomass generated yearly, Malaysia has a potential to utilize the biomass efficiently and effectively as an alternative energy source to replace fossil fuels (Shuit *et al*., 2009; Sumathi *et al*., 2008)

1.3 Problem Statement

Raw biomass has low energy density compared to fossil fuels, so large amount of biomass are needed. In addition, it is hard to grind the biomass and it can be very costly. Raw biomass also have a hygroscopic behaviour which is it cannot be stored for long time. Because of those problems, pretreatment of biomass is needed, and the method that suitable and compatible with characteristic of biomass is torrefaction.

Biomass torrefaction has been recognized as a technically feasible method for converting raw biomass into high-energy-density, hydrophobic, compactable, grindable, and lower oxygen-to-carbon (O/C) ratio solid (Tumuluru *et al*., 2010). In torrefaction process, it was strongly depended on the thermal decomposition behavior and lignocellulosic constituents. In order to identify the decomposition regions of palm oil and evaluate kinetic parameters, and mass changes, thermogravimetric analysis (TGA) can be used. In this work, PKS, EFB, mersawa sawdust and durian were used.

1.4 Objective

The objective of this research is to study the thermal decomposition and characterization of palm oil waste and forestry residues during torrefaction process.

1.5 Scope of this research

The scope of this study will focus on decomposition profile/region within hemicellulose, cellulose, and lignin of the palm oil waste (PKS, and EFB), and forestry residue (wood waste, and sawdust). Sample mass must in the range ±5mg, the temperature must not over than 600 ºC, and heating rate were used are 10 ºC and 20 ºC/min Palm kernel shell (PKS) is a by-product from production of kernel oil. Palm kernel nut contain kernel oil was cracked down to kernel and kernel shell. Meanwhile fresh palm oil fruit bunch (FFB) after went through steam heating is put under threshing process, which separate palm fruit from its bunch, it become EFB (empty fruit bunch). Wood wastes are a by-product from wood-processing industries, such as sawdust, shavings, chips, and barks. To use this biomass, it was grinded and sieved to particle size of 500-630µm. To study thermal decomposition and characterization of biomass, this experiment was performed under nonisothermal conditions in standard TGA (TGA Q500, from TA instrument).

1.6 Organisation of this thesis

Chapter 2 provides a description about the biomass. A general description, characteristics of the biomass, and type of biomass used will be explained. In this chapter also provides a brief explanation of the torrefaction and thermal decomposition. Then, thermogravimetric analysis of the biomass will be discussed. A summary of the previous experimental work on thermal decomposition of biomass is also presented.

Chapter 3 gives a review of the biomass used for thermogravimetric analysis and provide the procedure to prepare the biomass samples and to run the experiment by using thermogravimetric analysis (TGA). Flow diagram will be included.

Chapter 4 will discuss about the result of this research. Discussion on the result will cover for all the scope of this study, which is the weight loss, decomposition region between the lignocellulosic components, and characteristic of biomass.

2 LITERATURE REVIEW

2.1 Overview

This chapter will discuss about general description or characteristics of biomass, and type of biomass used which are PKS, EFB, wood waste, and sawdust. In this chapter also provides a brief explanation of the torrefaction and then, thermogravimetric analysis of the biomass also will be discussed. A summary of the previous experimental work on thermal decomposition of biomass is also presented.

2.2 Biomass

Biomass is biological material derived from living, or recently living organisms. It most often refers to plants or plant-based materials which are specifically called lignocellulosic biomass. The main components of lignocellulosic biomass samples are cellulose, hemicellulose, and lignin. Biomass (solid waste) that come from fresh fruit bunch of palm oil are empty fruit bunch (EFB), palm mesocarp fibre (PMF), palm kernel shell (PKS), palm kernel cake (PKC), and palm oil mill effluent (POME). Meanwhile, forestry residues such as sawdust, dead wood, waste wood, and etc. are the biomass material that remained in forest and has been harvested for timber, including logging residues, excess small pole trees, natural attrition, and extracting stem-wood for pulp.

Biomass is a promising alternative source to replace fossil fuels as it releases the energy in the form of heat during combustion. It is the only one renewable energy source of carbon that can be converted into convenient solid, liquid, and gaseous fuels through different conversion process (Ahmed *et al.*, 2011). However raw biomass have characteristics that cause a barrier in order to utilize it as a biofuels such as high moisture content, low energy density compared to fossil fuels, hygroscopic behavior that it cannot be stored for a long time, and poor grindability, therefore pretreatment of biomass required (Chen & Kuo, 2010; Arias *et al.*, 2008). Pretreatment via torrefaction is chosen because of suitability with the characteristic of biomass.

2.3 Utilization of biomass in Malaysia

Utilization of biomass discussed by Adlansyah (2014) is in the form of thermal conversion or biological conversion. For thermal conversion, biomass is mainly utilized in term of power or electricity generation where it is commercially used in industry which is biomass are incinerated to generate heat energy for boiler or steam turbines of palm oil mills and for landfills known as methane combustion. Meanwhile, biological conversion is to produce bioplastic, methane generation, bio-compost, organic acid, and animal feedstock (Mohd Ali *et al.*, 2010).

From the objectives of the third outline perspective plan (OPP3) (2001-2010) and the eighth Malaysia plan (2001-2005), to encourage and enhance the uses of renewable sources of energy (RE), the Government has developed several strategies to strengthen and develop the use of RE as an energy source fifth countries. For the implementation of the ninth Malaysia Plan (9MP), the government has set a target of generating electricity by grid connected using RE sources such as; biomass, biogas, mini-hydro, wind, solar and municipal waste in the capacity of 350MW, which involves 300MW and 50MW in peninsular Malaysia, Sabah. One of the renewable energy projects is biomass energy project.

Ministry of energy, water and communications has received a facility from global environment facility (GEF) to develop a project for the national programme for “Biomass-based power generation and co-generation” (Biogen) in the Malaysia palm oil industry. The main objective of this project is to determine and overcome all the obstacles in the country’s effect to commercialize the use of waste biomass co-generation, including power generators’ grid connected in Malaysia (KeTTHA, 2015). **Table 2-1** shows that energy potential get from certain amount of residue or biomass.

Table 2-1: Energy potential from biomass (data from 2011)

Residue	Amount (tonne)	CV (MJ/kg)	Energy Potential (MW_{th})
EFB	24.5 million	14.6	10,436
PKS	6.1 million	19.0	3,660
Sawdust	14.9 million	11.6	5,977

The government of Malaysia has set a target to increase its biomass power generation capacity to 800MW by 2020 (KeTTHA, 2015; Wendy *et al.*, 2012). However, there are several barriers of biomass utilization which are in term of policy, it is a limited incentives on biomass utilization. In term of supply and demand perspectives, no reliable data on actual potential of biomass, slow implementation of 5th Fuel Policy (RE, including biomass) and limited effort to regulate and enforce biomass programs.

In addition, biomass utilization facing with financial and technical barriers and also institutional barrier which are, in order to utilize biomass, high initial investment is needed, limited local technologies and equipment, financial support is poor (no record on biomass industry) and limited coordination among the local agencies. Major challenges of biomass energy in Malaysia are electricity sales price, renewable energy power purchasing agreement, lack of promotion, and subsidy for conventional energy (Mohd Ali *et al*., 2010).

2.4 *Palm oil waste*

Palm oil waste such as PKS, EFB, PKC, PMF, and POME are generated 90% from palm oil tree as shown in **Figure 2-1** and other 10% is the oil product.

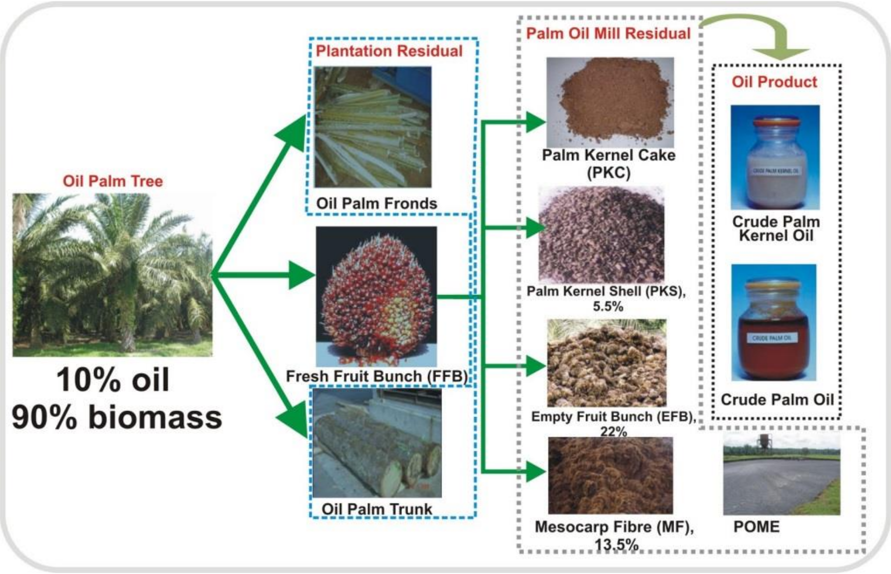

Figure 2-1: Infographic of biomass from palm oil tree

Typically, palm oil waste contain 40 – 60 wt% cellulose, 20 – 40 wt% hemicellulose, and 10 – 25 wt% lignin on dry basis.

2.4.1 Palm kernel shell (PKS)

The PKS is known as “virgin biomass”, and it is a by-product from production of kernel oil as shown in **Figure 2-2**. PKS is carbonaceous solids which is contain high volume percentage of carbon element and can be converted as a heat energy source by thermal reaction (Najmi *et al.*, 2014). **Table 2-2** below shows the element composition of PKS.

Figure 2-2: Palm kernel shell

Table 2-2: Composition of PKS

Item	Value (Typical)	Test Method
Moisture	17.0%	ASTM D 3302-05
Ash	3.0%	ASTM D 3174-02
Sulphur	0.09%	ASTM D 4239-02
Chlorine	0.05%	ASTM D 2361-02
Calorific Value	3800 Kcal/Kg	ASTM D 5865-02
Impurities	<1%	Gravimetric
Bulk Density	600 Kg/m^3	

(Nordic Bio Fuel, 2014) *ASTM = American Society for Testing and Material.

PKS also can be used for daily cooking, as it burned without recovery of energy. Besides that, it also used to cover the surfaces of the roads in the plantation areas. According to Khan *et al.*, (2011), typical properties of lignocellulosic of PKS (wt% dry basis), hemicellulose contain 22.7 wt%, cellulose contain about 20.8 wt%, and lignin contain approximately 50.7 wt%.

2.4.2 Empty fruit bunch (EFB)

About 20,000 tonnes of Fresh fruit bunch (FFB) per month by a mill processing would produce approximately 4,600 tonnes of EFB. After fresh fruit bunch went through steam heating and put under threshing process, it will become EFB as shown in **Figure 2-3**.

Figure 2-3: Empty fruit bunch (EFB)

Value of composition such as element compound, moisture, ash, cellulose, hemicellulose and lignin in EFB is shown in **Table 2-3**.

Table 2-3: Composition of EFB

Item	**Value (wt% dry basis)**
Moisture	84.61
Ash	5.50
C	40.73
H	5.75
N	1.40
S	0.22
O	51.90
Cellulose	38.30
Hemicellulose	35.30
Lignin	22.10
Volatiles	84.61

(Khan *et al*., 2011)

EFB is incinerated into potash-rich ash as potassium fertilizer, shredded and dehydrated palm oil mulching to 50% moisture content for used as boiler fuel or raw EFB used as solid fuel for steam boiler. Besides that, fibers of EFB used to produce neutral sulphate semi chemical pulps, sulphate, papers, thermo mechanical pulps, bio-oil through pyrolysis process and particle boards (HURFAR, 2014).

2.5 Forestry residues

Biomass material remained in forest that has been harvested for timber, including logging residues, excess small pole trees, natural attrition, extracting stem-wood for pulp and a rough or rotten dead wood are called forestry residues as shown in **Figure 2-4**. These residues can be collected after a timber harvest and used for energy purposes. The advantage of using forest residues is, an existing collection infrastructure is already set up to harvest wood in many areas (EPA, 2014). Forest residues normally have a low density.

Figure 2-4: Example of forestry residues

The biomass material usually have moisture content in the range 30 – 60 wt%, it's depend on type, location, time harvest and period of storage after harvest. Bulk density in the range 50 – 400 kgm^{-3} and it is usually will have only moderate flow properties, but will readily permit through-circulation of the drying medium (Fagernas *et al.,* 2010).

Diomides *et al.,* (2013) studied that the chemical composition on hybrid poplar clones generally contained 39 wt% cellulose, 21 wt% hemicellulose, 27 wt% lignin, 1.3 wt% ash. Then, typical compositions for softwood are about 40 – 44 wt% of cellulose, 25 – 29 wt% of hemicellulose, and 25 – 31 wt% of lignin. Meanwhile, typical compositions for hardwood are 43 – 47 wt% of cellulose, 25 – 35 wt% of hemicellulose, and 17 – 23 wt% of lignin (Peng, 2012).

2.6 Thermogravimetric analysis of biomass

Knowledge of the chemical composition, thermal behaviour and reactivity of biomass can be known from thermoanalytical techniques such as thermogravimetric analysis (TG) and derivative thermogravimetry (DTG). Thermogravimetric analyses are based on the volatilization rate of fuels, which is dependent on the heating rate applied to the sample and the type of fuel. TG methodologies also based on small samples obtained from large batches (Jose *et al.,* 2010). Results from TG were compared to the thermal degradation of biomass, however the information provided is only about overall weight loss of the sample in relation to temperature, which is not necessarily correspond to the complex chemical reaction in the thermal degradation of biomass. TGA is an analytical technique which records the loss of the weight of the sample as the temperature raised at a uniform rate. Example of general TGA curve is shown in **Figure 2-5**. In addition, TGA also has been extensively used to determine the characteristic of devolatilisation and also to determine kinetic parameters (Paul & Besler, 1993)

There are three decomposition stages involve, the first stage usually occurs when temperature at below 200 ºC. It is correspond to drying period where light volatiles, mainly water were liberated throughout the procedure. Second stage is devolatilization, where the major step in all thermo-chemical conversion process involving biomass take place. This stage of decomposition usually occuring at temperature between 200 ºC to 500 ºC where remarkable slope of TG curve are observed, and corresponding to significant drop in weight of sample due to liberation of volatile hydrocarbon of hemicelluloses, cellulose, and some part of lignin. Last stage is where the weight loss is not as momentous as in stage two, primarily due to the steady decompistion of the remaining heavy components mainly from lignin (Shinde & Singervelu, 2014).

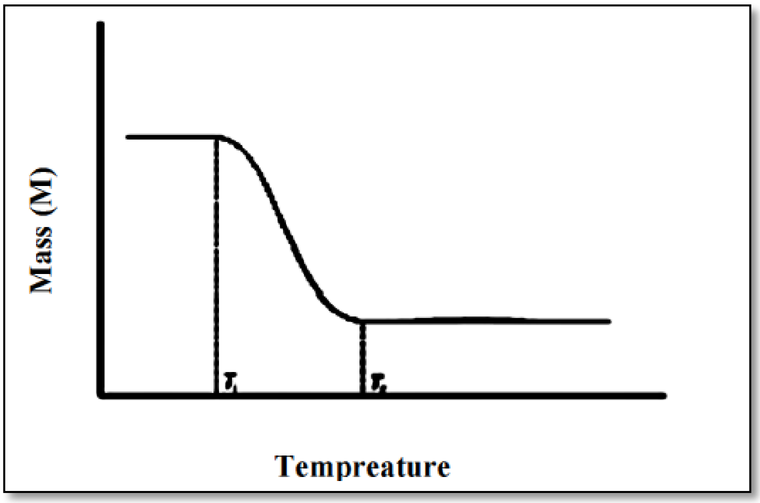

Figure 2-5: General TGA curve line

2.7 Torrefaction by using thermogravimetric analysis (TGA)

Torrefaction is a process used to produce high-grade solid biofuels from biomass and basic principle of torrefaction is shown in **Figure 2-6**. Torrified biomass has high calorific value, more homogeneous product, higher bulk density, excellent grindability durability, hydrophobic nature or water resistance, and no biological activity. Torrefaction is a mild pyrolysis, thermal process that involves heating the biomass to temperatures between 200 – 300 ºC, at atmospheric pressure and absence of oxygen (Tumuluru *et al.*, 2010; Muafah *et al*., 2012; DTI, 2012).

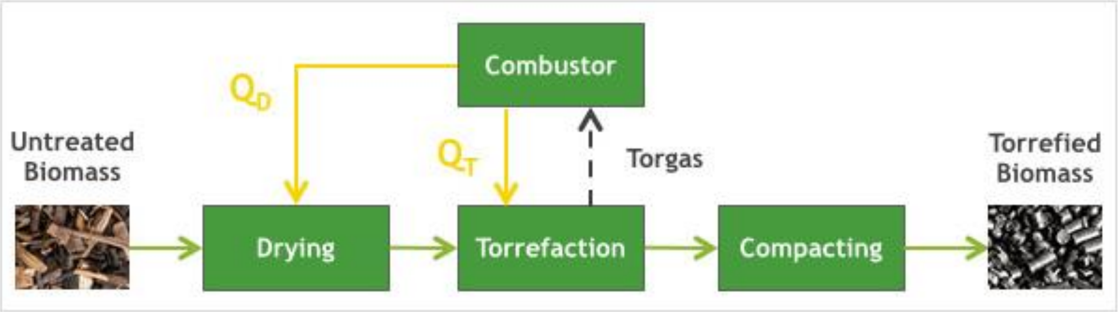

Figure 2-6: Basic for principle (Topell, 2001)

Product of torrefaction consist of dark color solid, condensate including moisture, acetic acid, and gases which are CO_2, CO and small amount of CH_4 and H_2 (Sabil *et al.*, 2013). This process strongly depended on the decomposition temperature of lignocellulosic component in biomass (Suzana *et al.,* 2011). In this work, during torrefaction process, the mass loss distributions for all types of biomass will be monitored by thermogravimetric analyzer (TGA). TGA was employed to understand the interaction between ionic liquids and biomass components. TGA provide information on thermal decomposition profile of respective components (Zhang *et al.*, 2013; Michael *et al.,* 2007).

Thermal decomposition of the hemicellulose, cellulose, and lignin is important because they influence the basics of thermochemical conversion process such as pyrolysis, combustion and gasification (Khan *et al.,* 2011). From the previous study, decomposition region that first to decompose is hemicellulose followed by cellulose and then lignin being last to decompose (Demirbas, 2001). According to Guo & Lua (2001), lignin is the last to decompose due to its heavy cross linked structure.

Decomposition temperature that proposed by Yang *et al.*, (2004) is in the range of 220 – 300 ºC for hemicellulose, 300 – 400 ºC for cellulose, and higher than 400 ºC decomposition of lignin observed. Meanwhile Khan *et al.,* (2011) studied that hemicellulose decompose in the range of 280 – 300 ºC, 340 – 360 for cellulose. Khan *et al.*, (2011) propose that there is no lignin decomposition observed. According tu Arias *et al.*, (2007), decomposition of lignin occur at 250 – 500 ºC, meanwhile hemicellulose decompose at temperature of 150 – 350 ºC, and cellulose decompose at 275 – 350 ºC. Decomposition of cellulose begin at 240 – 350 ºC, decomposition of hemicellulose occurs in the range of 130 – 260 ºC, and lignin decomposes when heated to 280 – 500 ºC (Tumuluru *et al.*, 2010).

The biomass with the high content of lignin is the most difficult to be decomposed, but biomass with the high content of hemicellulose much easier to be decomposed because the hemicelluose can enhance the decomposition rate. The torrefaction of biomass will be affected by decomposition temperature of hemicellulose, cellulose, and lignin.

2.8 Torrefaction in Malaysia

In Malaysia, there are several companies that doing some practices on torrefaction of biomass such as C.H.E Group, and ASPIRE ENERGY Sdn Bhd (AESB). On May 2012, C.H.E Metal Works Sdn Bhd (CHE Group) announces strategic partnership with ERK Eckrohrkessel GmbH (ERK), The Fitzpatrick Company (Fitzpatrick) and Torftech Ltd to intensifying cooperation between four engineering companies to develop the biomass pretreatment and power generation equipment including processes. C.H.E also working together with local academy to do feasibility and lab analysis to develop complete biomass pretreatment and power generation plant (GSIAC, 2012).

Meanwhile, ASPIRE ENERGY Sdn Bhd (AESB) offer technology that produce torrefied biocoal pellet which is derived from biomass residual. AESB using R-02 torrefaction technology, it is a patented method that use dry super heat steam (SHS) as the heating medium to perform the drying and torrefaction process. As a mild thermal pyrolysis in SHS atmosphere by using temperature between 240 ºC – 280 ºC, it converts the waste into Biofuel. Then, Biofuel is then “cooled” to below 130 ºC for discharge and ready for grinding, and densification.

In 2011, Russian energy giant and Gazprom has signed Memorandum of Understanding with a major Malaysia company to purchase torrefied palm residues to generate electricity (bioMass.sp, 2011). However, research on torrefaction of biomass in Malaysia is still on progress to further understand it mechanism. According to (Amin *et al.*, 2011), torrefied temperature used to get higher heating value, high carbon and ash content, is 280 ºC within 90 minute. Then, according to Yoshimitsu *et al.*, (2011) torrefaction in the presence of oxygen can be carried out without any significant probems. A maximum 7% of biomass was lost through complete oxidation at 15% of oxygen.

3 MATERIALS AND METHODS

3.1 Overview

In this work, four type of biomass were used, which are PKS, and EFB from palm oil waste, and sawdust from forestry residues. The raw biomass was collected at kilang sawit LCSB Lepar, and Federal Sawmill Sdn Bhd in Gambang, Kuantan. This chapter discuss about method for preparation of biomass samples and procedure of torrefaction by using TGA.

3.2 Preparation of biomass samples

3.2.1 Palm oil waste samples preparation

PKS and EFB were collected at kilang sawit LCSB Lepar in Gambang, Kuantan. Both materials were dried at 105 ºC with moisture content left is less than 10%. After drying process, the raw materials were grinded and sieved to a particle size of 500 – 630µm as shown in **Figure 3-1**.

Figure 3-1: PKS and EFB after sieving

3.2.2 Forestry residues samples preparation

Mersawa and durian sawdust sample were collected at Seng Peng Sawmill Sdn Bhd in Gambang, Kuantan. Sample was dried at 105 ºC until moisture content left is less than 10%. After drying, sawdust sample was sieved to a particle size of 500 – 630µm as shown in **Figure 3-2**.

Figure 3-2: Mersawa and durian sawdust after sieving

3.3 Heating value by using bomb calorimeter

Higher heating value (HHV) of material was determined by using oxygen bomb calorimeter as shown in **Figure 3-3**. 10 cm of fuse wire was used and fuse wire was attached to the bomb head through the eyelet holes. Then, approximately 0.5 gram of biomass was placed into the capsule. About 2 litre water was inserted into the calorimeter bucket. After bomb head was placed in the cylinder, oxygen was filled in the cylinder by connecting oxygen filling connection onto the check valve on the bomb head. Oxygen was filled until the meter show the value of 20, then, the valve on the regulator was turned off. The bomb was inserted into the bucket by using lifting handle, the cover of the calorimeter bucket was closed and the thermometer was lowered. Stirrer was switched on, and after 1 minute, the power button was switched on. The values of temperature of every 1 minute interval were recorded until the value is constant. When the value of temperature is constant, the machine was turned off and then, the length of unburned fuse wire was measured. Then, HHV was calculated by using **equation 4.1.2**.

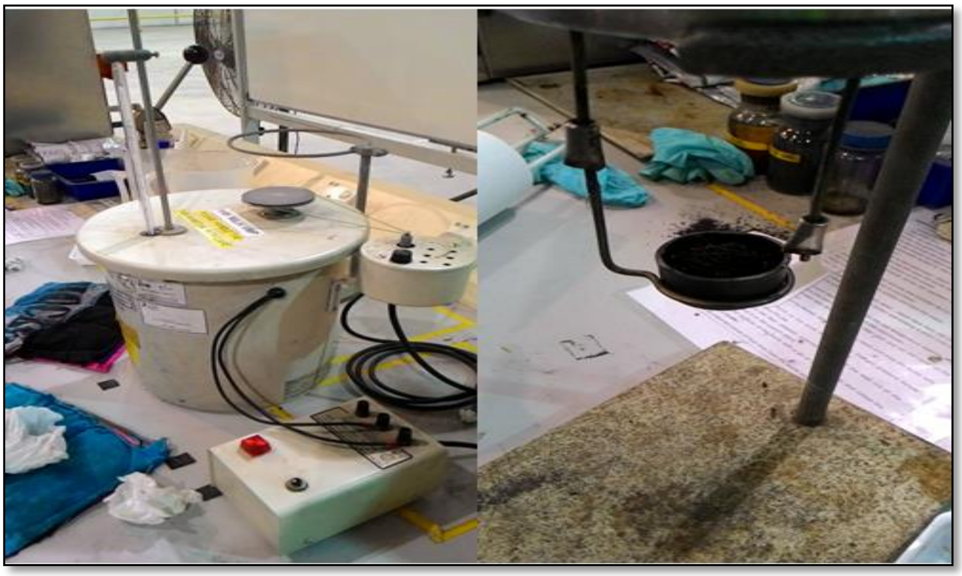

Figure 3-3: Bomb calorimeter

3.4 Torrefaction by using TGA

Biomasses were torrified by using TGA Q500 as shown in **Figure 3-4**. Samples were weighed approximately 5mg. Before start of each experiment, the systems was purged with N_2 gas at 100ml/min for about 30 min (at 50 ºC) to remove entrapped gases. The samples were heated with different constant heating rate at 10 ºC/min and 20 ºC/min. The initial temperature was set at 30 ºC and final temperature was set at 600 ºC. Air cool for 50 min, and data sampling interval set at 0.50 s/pt. The weight loss and maximum conversion temperature were discussed. The observation was observed only between the temperatures at 200 ºC to 300 ºC.

Figure 3-4: Thermogravimetric analyzer (TGA Q500)

4 RESULTS AND DISCUSSIONS

4.1 Overview

In this chapter, results of this experiment are discussed. Besides that, in this topic also show how to calculate moisture content each sample, and the heating values before TGA and after TGA are calculated. Moisture content is calculated by using formula;

$$\boldsymbol{M_C} = \left[\frac{(\boldsymbol{W_W} - \boldsymbol{W_d})}{\boldsymbol{W_W}}\right] \times \mathbf{100}\% \qquad \textbf{(4.1.1)}$$

Where,

M_C = Moisture content (%) of material
W_w= Wet weight of the sample
W_d = Weight of the sample after drying

Then the formula to calculate high heating value is;

$$\boldsymbol{H_g} = \frac{\boldsymbol{tW} - \boldsymbol{e_1} - \boldsymbol{e_2} - \boldsymbol{e_3}}{\boldsymbol{m}} \qquad \textbf{(4.1.2)}$$

Where,

t = temperature rise / difference
W= 2409.26 cal/ ºC
e_1= correction in calories for heat of formation of nitric acid (HNO_3)
e_2= correction in calories for heat of formation of sulphuric acid
e_3= correction in calories for heat of combustion of fuse wire
(2.3× centimetres of fuse wire consume in firing)
m= mass of sample (0.5 ± 0.0008 g)

Correction in calories for heat of formation of nitric and sulphuric acid is neglected. (Thermofluids Laboratory, 1999)

Moisture content for all sample were approximately less than 10 % with high heating value shown in **Table 4-1**.