BIOCHAR FROM OIL PALM EMPTY FRUIT BUNCHES AND OIL PALM SHELLS VIA SLOW PYROLYSIS

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by

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LIST OF SYMBOLS

Å	angstrom
°C	degree celcius
°C/min	degree celcius per minute
cc/g	centimeter cubic per gram
dM/dT	rate of change of mass
m^2/g	meter squared per gram

LIST OF ABBREVIATION

AIM	Agensi Inovasi Malaysia
ASTM	American Society for Testing Material
BET	Brunauer, Emmett and Teller
C	carbon
Ca	calcium
CH_4	methane
Cl	chlorine
CO	carbon monoxide
CO_2	carbon dioxide
daf	dry-ash-free
db	dry basis
db wt %	dry basis weight percentage
DTG	derivative thermogravimetric
ECN	Energy Research Centre of the Netherlands
EFB	Empty Fruit Bunches
FELCRA	Federal Land Consolidation & Rehabilitation Authority
FELDA	Federal Land Development Authority
g	gram
GHG	greenhouse gas
h	hour
H	hydrogen
ha	hectare
IBI	International Biochar Initiative
IEA	International Energy Agency
K	potassium
mf wt %	moisture free weight percentage

min	minute
mL	milliliter
N	nitrogen
Na	sodium
NO_2	nitrous oxide
O	oxygen
OPS	Oil Palm Shell
REN21	the Renewable Energy Policy Network for the 21st Century
RISDA	Rubber Industry Smallholders Development Authority
SEM	scanning electron microscopy
Si	silicon
TG	thermogravimetric
USDA	United States Department of Agriculture
wt	weight
wt %	weight percentage

BIOARANG DARIPADA TANDAN BUAH KOSONG KELAPA SAWIT DAN TEMPURUNG KELAPA SAWIT MELALUI PIROLISIS PERLAHAN

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan bioarang daripada tandan buah kosong kelapa sawit (EFB) dan tempurung kelapa sawit (OPS) melalui proses pirolisis perlahan berskala makmal, menyiasat ciri - ciri bioarang yang dihasilkan daripada pelbagai keadaan bahan mentah dan proses pirolisis, dan membandingkan bioarang yang dihasilkan daripada EFB dan OPS. Analisis awal telah dijalankan terhadap kedua - dua bahan mentah untuk mengkaji ciri - ciri bahan. Pra-rawatan basuhan menggunakan air telah dilakukan terhadap bahan mentah EFB untuk mempelbagaikan kandungan abu bahan mentah. Untuk bahan mentah EFB, kesan tempoh masa dan kandungan abu bahan mentah terhadap hasil bioarang dan ciri - cirinya telah disiasat. Tempoh masa telah diubah dari 0.5 jam hingga 4.0 jam, sementara suhu dan kadar pemanasan masing - masing ditetapkan pada 550 °C dan 5 °C/min. Bahan mentah EFB yang mempunyai kandungan abu dalam linkungan 1.60 hingga 5.29 mf wt % telah dipirolisis pada suhu 550 °C dan kadar pemanasan 5 °C/min selama 1 jam. Untuk bahan mentah OPS, kesan suhu dan tempoh masa terhadap hasil bioarang dan ciri - cirinya telah dikaji. OPS telah dipirolisis pada 6 suhu yang berbeza; 400 °C, 450 °C, 500 °C, 550 °C, 600 °C and 650 °C pada kadar pemanasan 5 °C/min selama 1 jam. Seterusnya, tempoh masa diubah dari 0.5 jam hingga 4.0 jam, sementara suhu dan kadar pemanasan masing - masing ditetapkan pada 550 °C dan 5 °C/min. Hasil bioarang, cecair dan gas ditentukan. Bioarang dianalisa melalui analisis proksimat, analisis unsur, kajian morfologi permukaan dan analisis luas kawasan permukaan BET. Didapati bahawa tempoh masa memberikan pengaruh kecil terhadap hasil produk untuk kedua - dua bahan mentah EFB dan OPS. Tempoh masa optimum bagi penghasilan bioarang daripada bahan mentah EFB dan OPS adalah masing - masing pada 1.0 jam dan 4.0 jam. Apabila suhu pirolisis ditingkatkan, hasil bioarang OPS berkurangan manakala kandungan karbon tetap dan luas kawasan permukaan

BET meningkat. Pengurangan kandungan abu bahan mentah EFB melalui proses pra-rawatan basuhan mendorong kepada pengurangan hasil bioarang dan peningkatan kandungan karbon tetap dan luas kawasan permukaan BET bioarang. Proses pirolisis perlahan bahan mentah OPS menghasilkan peratusan bioarang yang lebih tinggi berbanding bahan mentah EFB untuk tempoh masa dari 0.5 jam hingga 4.0 jam. Analisis ciri - ciri bioarang menunjukkan bioarang OPS mempunyai kandungan karbon tetap dan luas kawasan permukaan BET yang lebih tinggi berbanding bioarang EFB. Kajian ini menunjukkan bioarang OPS yang dihasilkan daripada proses pirolisis perlahan berskala makmal mempunyai kualiti yang lebih baik berbanding bioarang EFB.

BIOCHAR FROM OIL PALM EMPTY FRUIT BUNCHES AND OIL PALM SHELLS VIA SLOW PYROLYSIS

ABSTRACT

The objectives of this study are to produce biochar from oil palm empty fruit bunches (EFB) and oil palm shell (OPS) via laboratory-scale slow pyrolysis system, investigate the characteristics of biochar produced from various feedstock and pyrolysis conditions, and compare the biochar produced from EFB and OPS. The preliminary analysis was performed on both feedstocks to investigate their properties. The water washing pre-treatment was carried out on the EFB feedstock to vary the ash content of the feedstock. For the EFB feedstock, the impacts of holding time and feedstock ash content on the biochar yield and characteristics were investigated. The holding time was varied from 0.5 h to 4.0 h, while the terminal temperature and heating rate were fixed at 550 °C and 5 °C/min respectively. The EFB feedstock in the range of 1.60 to 5.29 mf wt % of ash content were pyrolyzed at 550 °C and 5 °C/min heating rate for 1 h holding time. For the OPS feedstock, the impacts of terminal temperature and holding time on the biochar yield and characteristics were studied. The OPS were pyrolyzed at 6 different terminal temperature; 400 °C, 450 °C, 500 °C, 550 °C, 600 °C and 650 °C at 5 °C/min heating rate for 1 h holding time. The holding time was then varied from 0.5 h to 4.0 h, while the terminal temperature and heating rate were fixed at 550 °C and 5 °C/min respectively. The biochar, liquid and gas yields were determined. The biochar was analyzed via proximate and elemental analysis, surface morphology study and BET surface area analysis. It was observed that the holding time had little influence on the product yields for both EFB and OPS feedstock. It was found that 1.0 h and 4.0 h are the optimum holding time for EFB and OPS biochar production respectively. As the terminal temperature elevated, the OPS biochar yield reduced while the fixed carbon content and BET surface area increased. The reduction of ash content in the EFB feedstock via water washing pre-treatment led to a decrease of biochar yield and corresponding increase of biochar's fixed carbon content and BET surface area. The slow pyrolysis of OPS feedstock produced higher biochar yield as compared to EFB feedstock for varied holding times between 0.5 h to 4.0 h. The analysis of biochar characteristics found that the OPS biochar contain higher fixed carbon content and has larger BET surface area as compared to the EFB biochar. This study shows that OPS biochar produced from the laboratory-scale slow pyrolysis process has better quality as compared to the EFB biochar.

CHAPTER ONE

INTRODUCTION

1.1 Research Overview

Energy is one of the core components in human daily life. It is related to economic development, nature sustainability and human civilization. It is required for meeting all of the basic needs such as food, health, agriculture, education, information and other infrastructure services (Rehling et al., 2004).

Energy could be obtained from both renewable and non-renewable resources. Currently, the main energy resource used by human is from non-renewable resources like fossil fuels. Coal, oil and natural gas are the three types of fossil fuels which can be used for energy provision. The formation of fossil fuels takes millions of years while the depletion process is faster than new ones are being made. Thus it cannot fulfill the energy demand which is increasing at an exponential rate due to the exponential growth of world population (Demirbas and Arin, 2002). The side effect from the utilization of fossil fuels causes a lot of problems in term of environmental sustainability. Fossil fuels burning increase the carbon dioxide (CO_2) concentration, one of greenhouse gases (GHG) in the atmosphere and causes global climate change. Climatic consequences such as desertification, a rise in ocean levels and increased number of hurricanes are among the ample evidences to show that the Earth is warming due to anthropogenic emissions of greenhouse gases (Lehmann, 2007a). Air pollution and contamination of groundwater are also the results from the use of fossil fuels. Thus, the transition to a sustainable renewable energy resource should be considered and encouraged to resolve the issue of future energy demand and environment sustainability.

1.2 Renewable Energy Scenario

In general, renewable energy is the energy generated from natural resources such as biomass, sunlight, wind, tides and geothermal heat which continually replenished. Renewable energy resources are reliable, sustainable and have the potential to provide energy services with zero or almost zero emission of both air pollutants and greenhouse gases (Demirbas, 2005, Manzano-Agugliaro et al., 2013). The utilization of renewable energy resources is possible to decrease the dependency on fossil fuel, increase the diversity of energy source option and increase the economic growth by providing new job opportunities. Besides, it can help to reduce the impact of greenhouse gases and climate change problems. The awareness about the nature sustainability enabled the renewable energy sector to grow and expand.

The percentage of global renewable energy consumption reported by the Renewable Energy Policy Network for the 21st Century (REN21) is illustrated in Figure 1.1. According to REN21, renewable energy resources have grown to supply an estimated 16.7% of global final energy consumption in 2010. It was estimated that 8.2% came from modern renewable energy resources like hydropower, wind, solar, geothermal, biofuels, and biomass. The other 8.5 % of total global energy was accounted for the traditional biomass which is used primarily for cooking and heating in rural areas of developing countries (REN21, 2012).

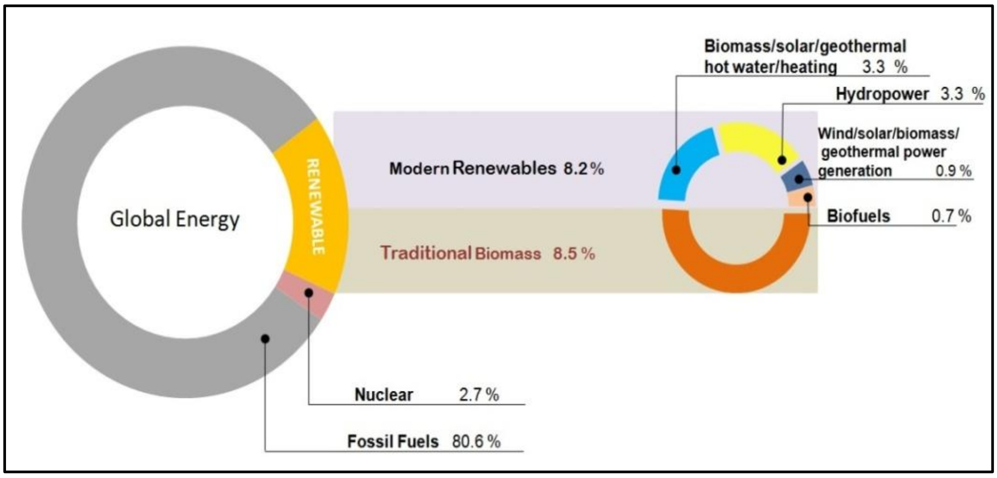

Figure 1.1: Renewable energy share of global final energy consumption in 2010 (REN21, 2012)

In 2011, it was reported that the global investment in the renewable energy power and fuels increased to $257 billion, which was more than six times of the total dollar invested in 2004 and 94% more than the total investment in 2007 (McCrone, 2012).

The utilization of renewable energy also draws great attention in Malaysia. The government had recognized the potential of renewable energy as an alternative to ensure the sustainability of energy resources. In the Eight Malaysian Plan (2001-2005), renewable energy was introduced as the Fifth Fuel (Ng et al., 2012). According to this plan, the renewable energy resources that will be promoted in terms of priority are biomass, biogas, municipal waste, solar and mini-hydro. The efforts of the utilization of renewable energy resources were further promoted in the Ninth Malaysian Plan from 2006 to 2010 (Mustapa et al., 2010).

Renewable energy resources are abundant in Malaysia. Currently, biomass and solar power are the renewable energy resources being exploited besides the primary energy sources such as oil, natural gas, hydro power and coal (Poh and Kong, 2002). Thus, to meet the high demand of energy supply in a sustainable manner, the concerted efforts on the implementation and development of renewable energy sector is required.

1.3 Biomass and Biochar

In general, biomass refers to forestry, purpose-grown agricultural crops, trees and plants, and organic, agricultural, agro-industrial and domestic wastes such as municipal and solid waste (Demirbas and Arin, 2002). According to Demirbas (2009), biomass term also includes gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic material. Biomass excludes organic material which has been transformed by geological processes into substances such as coal or petroleum (Aghamohammadi et al., 2011).

Biomass is known as one of the major world renewable energy resource. It is a suitable alternative to substitute the energy dependency on fossil fuel. According to Demirbas (2009), biomass appears as an attractive resource due to its ability to sustainably developed in the future. It has the attributes that contribute to a healthy environment and economy. Besides, the utilization of biomass offers great benefits towards the nature by reducing waste management problem and help in the climate change mitigation. It also has potential to contribute towards the positive economic growth.

Energy from biomass can be recovered via thermal, biological and physical process. Thermochemical conversion which includes combustion, gasification and pyrolysis process (Özçimen and Karaosmanoğlu, 2004, Bridgwater, 2003) is one of the most common routes applied to convert biomass into various form of energy. These conversion processes are described and classified by the type of final products obtained, the properties of the feedstock used and their operation parameters which include temperature, heating rate and holding time often known as residence time.

Biomass can be converted into solid char, liquid bio-oil and gas products via pyrolysis products. The gas or syngas produced from the pyrolysis process is composed primarily of hydrogen, carbon monoxide, carbon dioxide and gaseous hydrocarbons such as methane. The gas can be used to supply the energy requirement of pyrolyzer operation (Abdullah et al., 2010). The gas can be burned to provide the heat required by the pyrolysis system (Lee et al., 2013). The liquid product or known as bio-oil produced from the pyrolysis process may be required for further upgrade and improvement before it can be used as fuel. Meanwhile, char can be used as a solid fuel. It also can be applied to the soil as soil enhancer or soil amendment. The char produced for this purpose is known as biochar.

Generally, biochar is the black carbon and porous substance formed from slow pyrolysis process. It is produced specifically to be applied as soil amendment due to its unusual chemical and physical characteristics (Koide et al., 2011). The production of biochar was inspired from the fertility of black soil in Amazon which is known as Terra Preta.

The production and application of biochar into soil contributes many benefits towards the nature sustainability and economic growth. The application of biochar helps the nature to mitigate the climate change by carbon sequestration (Lehmann et al., 2006, Sohi et al., 2010a). Besides, the utilization of biomass such as agriculture residue, crop waste, wood chip and organic waste as the feedstock will reduce the waste management problems as well as the emission of the anthropogenic greenhouse gases like carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (NO_2) from the degradation of the dumped wastes (Lehmann et al., 2006). The addition of biochar into soil will improve the soil function by increasing water holding capacity (Glaser et al., 2002), increase soil organic carbon, neutralize soil acidity and increase soil pH (Chan et al., 2007). The improvement of soil quality then will increase the crop yield.

1.4 Oil Palm Biomass

Malaysia has a significant amount of agricultural activities. The abundant of biomass such as agricultural wastes could be turned into alternative source of renewable energy.

Oil palm biomass is one of the potential renewable energy resources identified by the Malaysia government. Oil palm wastes are high-potential biomass energy resources in Malaysia because Malaysia is the second largest producer and exporter of palm oil in the world. In 2012, up to 5.08 million hectares of land is cultivated with oil palm (MPOB, 2012). With the growth of oil palm industry, the amount of residues produced also shows a significant increment. The palm oil sector generates the largest amount of biomass, estimated at 80 million dry tonnes in 2010 and this amount is expected to increase about 100 million dry tonnes by 2020 as reported by Agensi Inovasi Malaysia (AIM, 2011).

Biomass obtained from oil palm industry include empty fruit bunches (EFB), oil palm shells (OPS), mesocarp fibers or pressed fruit fibers (PFF), oil palm fronds (OPF) and oil palm trunks (OPT). EFB, OPS and PFF are the oil palm wastes generated from the mills. Meanwhile, OPF and OPT are obtained from the field or plantations. The estimate of dry matter production of oil palm biomass based on the statistics of planted area and average yield of fresh fruit bunches (FFB) obtained from Malaysian Palm Oil Board (MPOB) is shown in Table 1.1.

Table 1.1: Estimates of dry matter production of oil palm biomass (Khor, 2009, MPOB, 2011, MPOB, 2013)

Year	**Biomass from mills**			**Biomass from fields**		**Total (mil. tonnes)**
	EFB (mil. tonnes)	**PFF (mil. tonnes)**	**OPS (mil. tonnes)**	**OPF (mil. tonnes)**	**OPT (mil. tonnes)**	
2003	5.559	5.848	3.375	40.31	3.971	59.063
2004	5.550	5.838	3.370	40.98	3.497	59.235
2005	5.889	6.195	3.575	42.84	3.643	62.142
2006	6.286	6.612	3.816	44.11	4.100	64.924
2007	6.308	6.636	3.830	45.78	5.170	67.724
2008	8.204	8.631	4.981	47.44	3.932	73.188
2009	6.935	7.295	4.210	50.11	6.809	75.359
2010	6.737	7.087	4.091	52.16	8.702	78.777
2011	7.581	7.974	4.603	53.24	6.397	79.795
2012	7.384	7.767	4.483	54.08	6.620	80.334

From Table 1.1, it can be observed that the total estimated amount of biomass generated from the mills and fields of the oil palm industry is increasing over the years. Most of the oil palm wastes such as OPF are left on the fields. Meanwhile, the solid biomass generated from the mill such as EFB is either to be used as organic fertilizer and soil cover material or dumped around the mill due to the high generation rate along with its limitation for current utilization (Paepatung et al., 2009).

Thus, the utilization of this abundant biomass resource as the feedstock to produce useful products such as biochar is a good way to reduce waste management problem. The sustainable utilization of the oil palm wastes also can be one of the ways to abate damage to the natural environment caused by fossil fuel consumption.

1.5 Problem Statement

The abundance of wastes generated from the palm oil industry in Malaysia shows a significant increment every year. The wastes such as EFB and OPS are mostly dumped in the mill area due to the high rate of wastes generation along its limited utilization. These wastes could be used as the feedstocks to produce biochar and therefore help minimize the waste management problem.

The emission of carbon dioxide, one of the anthropogenic greenhouse gases have risen by more than 3% annually (Ghani et al., 2013), and this resulted in a rapid rise in global temperature which resulted to the shift of weather patterns. Therefore, a new approach to maintain carbon in a stable from that can be stored outside the atmosphere for longer periods should be developed (Rebitanim et al., 2013). The production and utilization of biochar have been suggested as a promising way to reduce the percentage of carbon dioxide in the atmosphere.

The yield and characteristics of biochar are depends on various factors such as the feedstock type, chemical and structural composition of feedstock, operating parameter, heating rate, holding time as well as the type of reactor. Currently, a few studies have been carried out in Malaysia such as reported by Khor and Lim (2008), Khor et al. (2010), Khor (2012), Shafie et al. (2012b), Kong S.H. et al. (2012), and Abnisa et al. (2013) to characterize the biochar produced from oil palm wastes under different conditions. However, further studies should be conducted due to insufficient and incomplete data and information of biochar characteristics produced from oil palm wastes under different production conditions.

The study of biochar characterization is necessary because of their potential environmental applications such as soil amending and atmospheric carbon sequestration. It is also necessary in order to understand the type of biochar that can promote plant growth. This research will provide more understanding into the properties of biochar and the influence of its feedstock from which it is produced.

1.6 Objectives and Scope of Research

This research aims to produce biochar from slow pyrolysis of oil palm empty fruit bunches (EFB) and oil palm shell (OPS) using a laboratory-scale slow pyrolysis system and investigate the characteristics of biochar produced under different conditions. It covers the study of EFB and OPS feedstocks characterization, slow pyroysis experiments of EFB and OPS and the characteristics of EFB and OPS biochars. Two different parameters are applied for the slow pyrolysis experiments of each EFB and OPS feedstocks. For EFB, the effect of holding time and feedstock ash content are studied. Water washing pre-treatment is conducted to vary the ash content of EFB feedstock. For OPS, the effects of temperature and holding time are studied. The study of the effect of ash content is not conducted for OPS in this research because OPS feedstock has lower percentage of ash content as compared to the EFB feedstock.

The objectives of this study are listed as follows:

(i) To study the characteristics of the EFB and OPS feedstocks for slow pyrolysis process.

(ii) To apply pre-treatment process on feedstock including size reduction and drying process. Water washing pre-treatment is performed on the EFB feedstock only.

(iii) To investigate the impact of various parameters such as terminal temperature, holding time and ash content of the feedstock on biochar yield and its characteristics.

(iv) To identify the impact of washing treatment of EFB on biochar produced.

(v) To compare and study the characteristics of biochar produced from EFB and OPS.

1.7 Thesis Structure

This thesis consists of five chapters; Introduction, Literature Review, Methodology, Results and Discussions, and Conclusion and Recommendations.

Chapter 1 describes the brief introduction to energy, biomass and biochar. Simple details on the current scenario of renewable energy and oil palm sector also explained in this chapter.

Chapter 2 provides the detail information about the biomass, energy conversion technology, biochar and the utilization oil palm wastes as feedstock. The literature review from other researcher works on the applied methods and recent findings of topics above are presented.

Chapter 3 describes the details of materials used and experimental method in this study. This chapter also elaborates the method of characterization of feedstock and biochar.

Chapter 4 presents the data and results obtained from the slow pyrolysis experiments and related analysis such as proximate and elemental analysis of both feedstock and biochar. The effects of different parameters such as holding time, ash content and terminal temperature on the yield percentage and properties of biochar are discussed. The results obtained are compared to the findings of the literature in Chapter 2.

Chapter 5 summarizes and concludes the findings from this study. The recommendations for future works are also included.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter provides the background and review of biomass and its conversion technology, oil palm wastes and biochar.

The review of biomass discusses about the structure of woody biomass and composition of various types of biomass. It is followed by the potential and utilization of biomass as renewable energy resource. This chapter outlines the conversion technology used to convert the biomass into energy via different routes of conversion process including pyrolysis process.

This chapter also briefs the current scenario of oil palm industry in Malaysia and the utilization of the wastes from the oil palm industry. It reviews the studies of the pyrolysis process using the different types of oil palm wastes. In the end of this chapter, the definition and background of the biochar is introduced. It reviews the properties, benefits, production activities of biochar and the findings from the studies of pyrolysis of biomass for biochar production.

2.2 Biomass

Biomass is one of the renewable energy resources. Biomass generally refers to the organic matter that has stored energy from sunlight via photosynthesis process. Biomass includes all organic material that stems from plants including algae, trees and crops (McKendry, 2002a). Biomass can refer to non-fossilized and biodegradable organic material deriving from animals and microorganisms and also the domestic wastes such as municipal and solid wastes (Demirbas, 2009, Demirbas and Arin, 2002).

Biomass resources include the crops which were planted specifically for energy use and the residues or leftover wastes from the plants that are used for other purposes (Garza, 2007). Sugarcane, switchgrass, corn, wheat, soybeans and sunflowers are the examples of the biomass which were grown for energy use. Meanwhile, sawdust, paper mill sludge, agricultural wastes, leftover wood and garbage are the waste matter generated from forestry, agricultural and manufacturing industries which also appeared as a source for biomass energy.

The utilization of biomass as the feedstock for bioenergy production has attracted attentions due to its properties as a renewable resource that could be developed in a sustainable manner. Besides, it appears to have positive environmental properties resulting in no net release of carbon dioxide and very low sulfur content (Gheorghe et al., 2009). Moreover, biomass has the potential to make a large contribution to rural development in term of economic and social benefits.

2.2.1 Structure and Compositions

Biomass consists of a complex mixture of organic materials such as carbohydrates, fats and proteins, along with small amounts of minerals such as sodium, phosphorus, calcium and iron. For plant biomass, the main components consist of extractives, fiber or cell wall components and ash as shown in Figure 2.1.

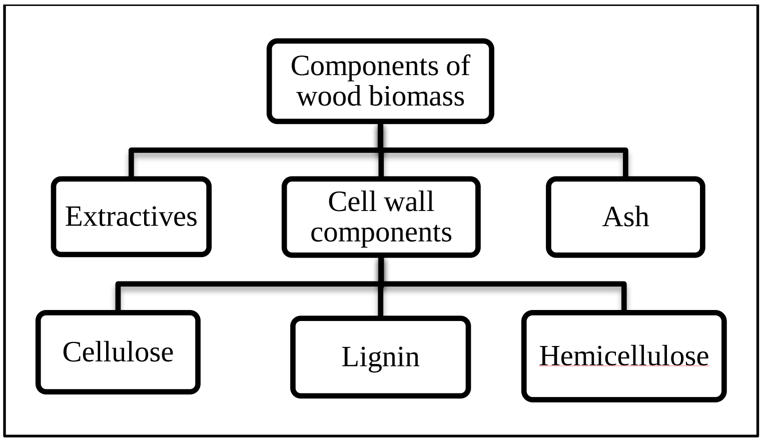

Figure 2.1 : Major constituents of a woody biomass (Basu, 2010)

Extractives are the substances that exist in the biomass tissues which function as intermediates in metabolism, as energy reserves and as defenses against microbial and insect attack (Mohan et al., 2006). It can be extracted by certain treatment with the polar or non-polar solvents and recovered by evaporation of the solution. Protein, oil, simple sugar, fat, waxes, starches and resin are the examples of the extractive.

Ash is the inorganic mineral component of biomass. The elements of ash present in biomass are Si, Ca, K, Na, Mg and small amount of S, P, Fe, Mn and Al (Raveendran et al., 1995). The percentage of ash content varies for different biomass as shown in Table 2.1. This percentage gives a remarkable impact during biomass energy conversion. Abdullah et al. (2007) found that yield of liquid product of fast pyrolysis process increased as the ash content of the empty fruit bunches feedstock was reduced via washing treatment. The highest yield for liquids produced from washed EFB (less ash content) was increased to be around 72% compared to liquids produced from unwashed EFB, which was about 55%. They also found that the reduction of ash content to less than about 3 mf wt % led to the production of homogeneous liquid.

Table 2.1: Composition of ash content in various type of biomass

Type of biomass	**Ash Content (db wt %)**	**Reference**
Bamboo sawdust	1.83	(Jung et al., 2008)
Oil palm empty fruit bunches (EFB)	7.54	(Omar et al., 2011)
Oil palm trunk (OPT)	10.30	(Lim and Lim, 1992)
Oil palm fiber (OPF)	7.00	(Lu et al., 2012)
Oil palm shell (OPS)	4.38	(Uemura et al., 2011)
Mesocarp fiber	3.32	
Rice husk	17.13	(Lin et al., 1998)
Apricot stone	1.41	(Özçimen and Ersoy-Meriçboyu, 2010)
Hazelnut shell	1.83	
Grapeseed	7.49	
Chestnut shell	1.59	

Meanwhile, cell wall components of wood biomass consist of cellulose, hemicelluloses and lignin. They are the three main constituents in the lignocellulosic material compositions. Cellulose is the primary structural component in the lignocellulosic biomass. Its molecular structure is shown in Figure 2.2. It is linear and remarkable pure organic polymer which consists solely of units of anhydroglucose. It is insoluble in water and most of organic solvent. The degradation occurs around 240 °C till 350 °C to produce anhydrocellulose and levoglucosan (Mohan et al., 2006). Cellulose also has a high strength due to the crystalline structure of thousands of units which are made of many glucose molecules (Basu, 2010).

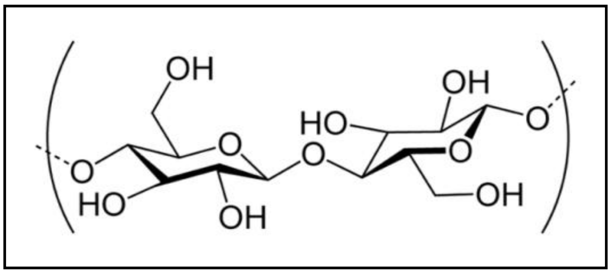

Figure 2.2: Molecular structure of cellulose

The cellulose molecules in the plant cell wall are interconnected by another molecule called hemicelluloses. It is also known as polyose. It is a mixture of various polymerized monosacharides such as glucose, mannose, galactose, xylose, arabinose 4-*O*-methyl glucuronic acid and galacturonic acid residues (Mohan et al., 2006). These main components are shown in Figure 2.3. Compared to cellulose, hemicellulose is a branched polymer and consists of shorter chains, has amorphous structure with little strength, soluble in weak alkaline solutions and degraded at 200 °C - 260 °C, thus tends to yield more gases (volatiles) and less tar than cellulose (Basu, 2010, Tiwari and Mishra, 2011).

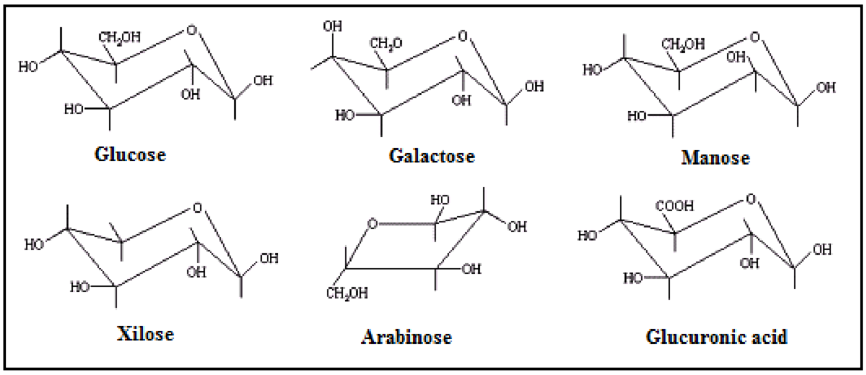

Figure 2.3: Main components of hemicelluloses

The other main constituent in lignocellulosic composition is lignin. It is a complex polymer which is built of hydrophenylprophane units. It functions as the main binder or cementing agent for the agglomeration of cellulose fiber component. Lignin decomposes when heated in the temperature range of 280 °C to 500 °C (Tiwari and Mishra, 2011). It is known as the most thermally resistant component compare to cellulose and hemicelluloses due to its complex chemical composition. According to Mohan et al. (2006), lignin pyrolysis produces more residual char than does the pyrolysis of cellulose.

Table 2.2 shows the percentage of cellulose, hemicelluloses and lignin of various types of biomass. It can be observed that the percentage of cellulose, hemicelluloses, lignin and extractive are varied for different type of biomass. The determination of this composition is important for a better understanding about the thermal conversion of lignocellulosic biomass. The cellulose contents of oil palm EFB found by Abnisa et al. (2013) is 51.2 % which is different with Omar et al. (2011). According to Omar et al. (2011), the dissimilarity of the composition of the same type of biomass might be due to the age and type of the plant as well as the location of the plantation from where the samples were obtained.

Table 2.2: Biochemical composition of various types of biomass fuels

Biomass	Hemicellulose	Cellulose	Lignin	Extractive	Notes and Reference
Almond shell	28.9	50.7	20.4	2.5	wt % daf (Demirbaş, 2002)
Hazelnut shell	30.4	26.8	42.9	3.3	
Olive husk	23.6	24.0	48.4	9.4	
Sunflower shell	34.6	48.4	17.0	2.7	
Walnut shell	22.7	25.6	52.3	2.8	
Tea waste	19.9	30.2	40.0	9.9	wt % dry (Demirbaş, 1997)
Wheat straw	39.1	28.8	18.6	n/a	
Oil palm EFB	21.6	23.7	29.2	n/a	wt % dry (Omar et al., 2011)
Mesocarp fiber	30.5	23.7	27.3	n/a	wt % (Abnisa et al., 2013)
Oil palm EFB	22.5	51.2	21.3	n/a	
Oil palm shell	21.6	27.7	44.0	n/a	
Bamboo	17.6	39.5	25.2	n/a	wt % (Antal et al., 2000)
Coconut shell	24.7	24.2	34.9	n/a	
Corn cob	25.2	26.3	16.3	n/a	
Garlic waste	6.9	24.2	8.5	n/a	
Oak wood	18.6	34.5	28.0	n/a	
Rice hull	16.8	30.9	35.9	n/a	

Note: n/a- not available

2.2.2 Potential and Utilization of Biomass

The abundance of wide range of biomass around the world makes it as a potential renewable energy resource. About 120 billion tonnes of biomass, the energy capacity of which is five times the total present energy consumption in the world, is formed each year by means of photosynthesis. However, only 1% of the total energy capacity has been used as energy (Mengjie and Suzhen, 1994). Photosynthesis is a process used by plants to convert light from the sun to chemical energy which is stored in the form of carbohydrate molecules. The list of potential biomass resources is listed in Table 2.3.

Table 2.3: Potential biomass as renewable energy resources (Wang and Keshwani, 2010)

Group of Biomass	Biomass	Details
Sugar Crops	Sugarcane	Used for ethanol production for gasoline-ethanol fuel blends and production of jiggery, refined sugar and alcoholic beverages.
	Sugar Beet	Grown commercially for sugar production due to high concentration of sucrose in its root.
	Sweet Sorghum	Used for production of sugar, syrup, fuel and roofing applications.
Starch Crops	Corn, wheat, potato Sweet Potato	Food sources.
Agricultural Residues	Corn stover, wheat straw, rice straw	Available for energy production and other value-added applications.
Herbaceous Biomass	Switchgrass	As the feedstock for solid, liquid and gaseous forms of energy.
	Mischantus	
	Coastal Bermuda Grass	
Woody Biomass	Hardwoods	Cultivated for direct combustion, gasification and production of briquettes.
	Softwoods	Dominant source of lignocellulosic materials (in northern hemisphere).
Oilseeds	Soybean	Food sources, medicinal and fuel purposes.
	Rapeseed (Canola)	Production of animal feed and vegetable oil.
	Sunflower	For oil production.
	Oil Palm	Production of edible oil.
	Waste Edible Oil	Leftover from oil that has been used in cooking foods.

In Malaysia, the plantation such as palm oil, rubber, cocoa, wood, timber, pineapple, coconut and pepper have the great potential to produce biomass residues (Shafie et al., 2012a). Other available biomass resources include empty fruit bunches, rice husk, sugarcane bagasse, manure, sawdust and grass crops. At least 168 million tonnes of biomass including municipal waste was produced annually (Ghani and Alias, 2013). Therefore, Malaysia has a great potential in turning the plentiful and abundant supply of biomass into renewable energy resource.

In general, biomass can be used for heat and power generation via burning process, digestion process to produce gas-like fuels such as methane and hydrogen and thermochemical conversion process such as pyrolysis and gasification (Demirbas, 2005). Biomass from the plantation usually is used as fuel to generate steam and electricity. For example, the bagasse is utilized as boiler fuels for the operation of sugar mills. (Shafie et al., 2012a). Oil palm wastes such as mesocarp fiber, shell, empty fruit bunches and the mill effluent are also used as the fuels for the boiler for fresh fruit bunches processing activity in the mill (Mahlia et al., 2001). It is also reported that the biomass becomes a major source of energy in a few foreign countries and numerous studies were carried out to develop ways of using biomass as an alternative to fossil fuels. For example, there is a large biomass plant found in Sweden, a large number of cars use alcohol to substitute petrol in Brazil and the attempts to develop power station which run solely on wood in United Kingdom (Demirbas, 2005).

The utilization of biomass as renewable energy resources offers a lot of benefits towards our nature and environment. It is one of the ways to reduce carbon dioxide (CO_2) from the atmosphere and help to mitigate climate change by reducing greenhouse gases. This can be achieved because biomass is derived from living plants that need CO_2 for its growth. The planting of plants will absorb CO_2 from the atmosphere via photosynthesis process. The production of biochar from biomass via pyrolysis process and the application of biochar into soil promote carbon negative effects because biochar systems can hold a substantial portion of carbon in soil, as compared to carbon neutral withdrawal by photosynthesis as shown in Figure 2.4. The normal or neutral carbon cycle on the left side of Figure 2.4 illustrates the carbon cycle in which the amount of CO_2 taken up by plants via photosynthesis is equal to the amount of CO_2 released back into the atmosphere by soil respiration. Meanwhile, in biochar carbon cycle, the agricultural wastes could be used as the feedstock for biochar production, and roughly half of the plant's carbon is retained as stable carbon in the biochar instead of being released to the atmosphere via decomposition or burning process. The application of biochar which is a carbon-rich material into the soil also will lock the carbon in soil for longer time. Thus, there is a net decrease of carbon in the atmosphere. The difference of the net carbon withdrawal from atmosphere by the normal photosynthesis system and biochar system is estimated about 20%. On the other hand, the utilization of biomass as renewable energy resources help to avoid the adverse environmental effects from the conventional methods of biomass residues disposal such as dumping and open air burning.

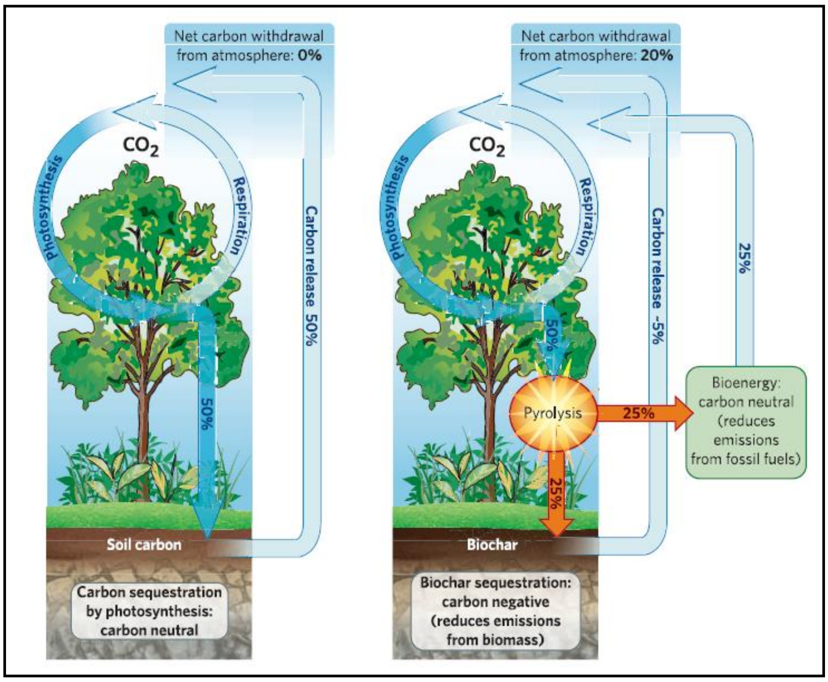

Figure 2.4: Comparison of normal carbon cycle and biochar carbon cycle (Lehmann, 2007b)

In term of social benefits, the utilization of biomass as renewable energy resources would improve life quality by reducing the harmful effect towards human health as compared with fossil fuel used. The development and implementation of biomass conversion technology also could offer local employment opportunities as well as introduce new skills and knowledge to society.

Therefore, with the potential and benefits offered, the utilization of biomass as renewable energy resources should be expanded to achieve higher consumption and application in the local and global market. The encouragement and support from the government and related organizations and agencies will overcome the barriers and open more opportunities for better implementation.

2.3 Biomass Conversion Technology

Biomass can be converted into energy by thermochemical, biological and physical processes. The choice of the appropriate conversion process is usually influenced by certain factors such as the type and quantity of biomass, the desired final products, environmental standards, economic conditions and project specific factors (McKendry, 2002b). Usually the desired final product is the main factor in the determination of the conversion routes. The details of the processes are described as follows:

a) Thermochemical Processes

Thermochemical process can be described as the modification of the physical and chemical properties of biomass by thermal interaction in a controlled environment (Titiladunayo et al., 2012). The thermochemical conversion process provides three main options to convert the biomass into various form of energy. They are combustion, gasification and pyrolysis.

Combustion is the process of burning the biomass in the air to obtain the energy in the form of heat, mechanical power or electricity. Demirbas (2004) reported that combustion is responsible for over 97% of the world bioenergy production. According to McKendry (2002b), this process is suitable for the biomass having the moisture content less than 50%. The biomass should undergo pre-drying treatment if it has higher moisture content. On the other hand, gasification is the process that converts the biomass into synthesis gas or called syngas which is a mixture of carbon monoxide, hydrogen and methane together with carbon dioxide and nitrogen under oxygen-deficient condition and occurs at the high temperature, generally higher than 700 °C (Bridgwater, 2003, Demirbas, 2004, Gautam et al., 2010). Pyrolysis process is described in details in the next section.

b) Biological Process

The conversion of biomass into energy such as fuels includes ethanol fermentation by yeast or bacteria and methane production by microbial consortia under anaerobic conditions (Miyamoto, 1997). Anaerobic digestion is a suitable way to convert high moisture biomass into a biogas which is a mixture of mainly methane and carbon dioxide. Meanwhile, the fermentation process is carried out commercially in many countries on a large scale for ethanol production from sugar crops such as sugar cane and sugar beet as well as the starch crops like maize and wheat (McKendry, 2002b).

c) Physical Process

Densification of the loose materials into a more compact form which includes pelletizing and briquetting is the process involved in the physical conversion process of biomass. The natural state of biomass usually have high moisture content, irregular shape and size and low bulk density, thus make it difficult to handle, transport, store and utilize (Lope Tabil et al., 2011) . Pelletizing and briquetting processes will make the biomass as the suitable feedstock for solid fuel.

2.3.1 Pyrolysis

Pyrolysis is one of the promising ways to convert biomass into various form of energy. It is a process of thermochemical degradation of the biomass at relatively low temperature around 500 °C to 800 °C (Nan et al., 1994, Bridgwater and Grassi, 1991) under limited or absence of oxygen. Goyal et al. (2008) reported that the pyrolysis of biomass may start at 350 °C to 550 °C and goes up to 700 °C . Meanwhile, the pyrolysis process of biomass such as wood can start at the temperature as low as 200 °C and lasts till 450 °C to 500 °C depending on its properties (Sinha et al., 2000). The pyrolysis of biomass produces the useful solid char, condensable liquids and gases. The proportion and compositions of these products varies according to the type of pyrolysis employed.

Babu (2008) claimed the pyrolysis mechanism started by the heat transfer to the solid particle surface of biomass by radiation and/or convection and then to the inside of the particle when the biomass is heated in an inert atmosphere. Next, the moisture removal in the biomass occurs due to the temperature increment within the biomass particle. The rise of temperature then initiated the pyrolysis process. The volatile and gaseous products flow through the pores of the particle during heat transfer process. The pyrolysis process proceeds with a rate depending on the local temperature. As the biomass converts into gases during the reaction, the pores of the solid particle becomes more porous. Thus, the enlarged pores provide many reaction sites to the volatile and gaseous products of pyrolysis and favor their interaction with the hot solid particle of biomass.

The general flow and changes that happen during the pyrolysis process as described by Sinha et al. (2000) and Mohan et al. (2006) can be simplified as shown in Figure 2.5.

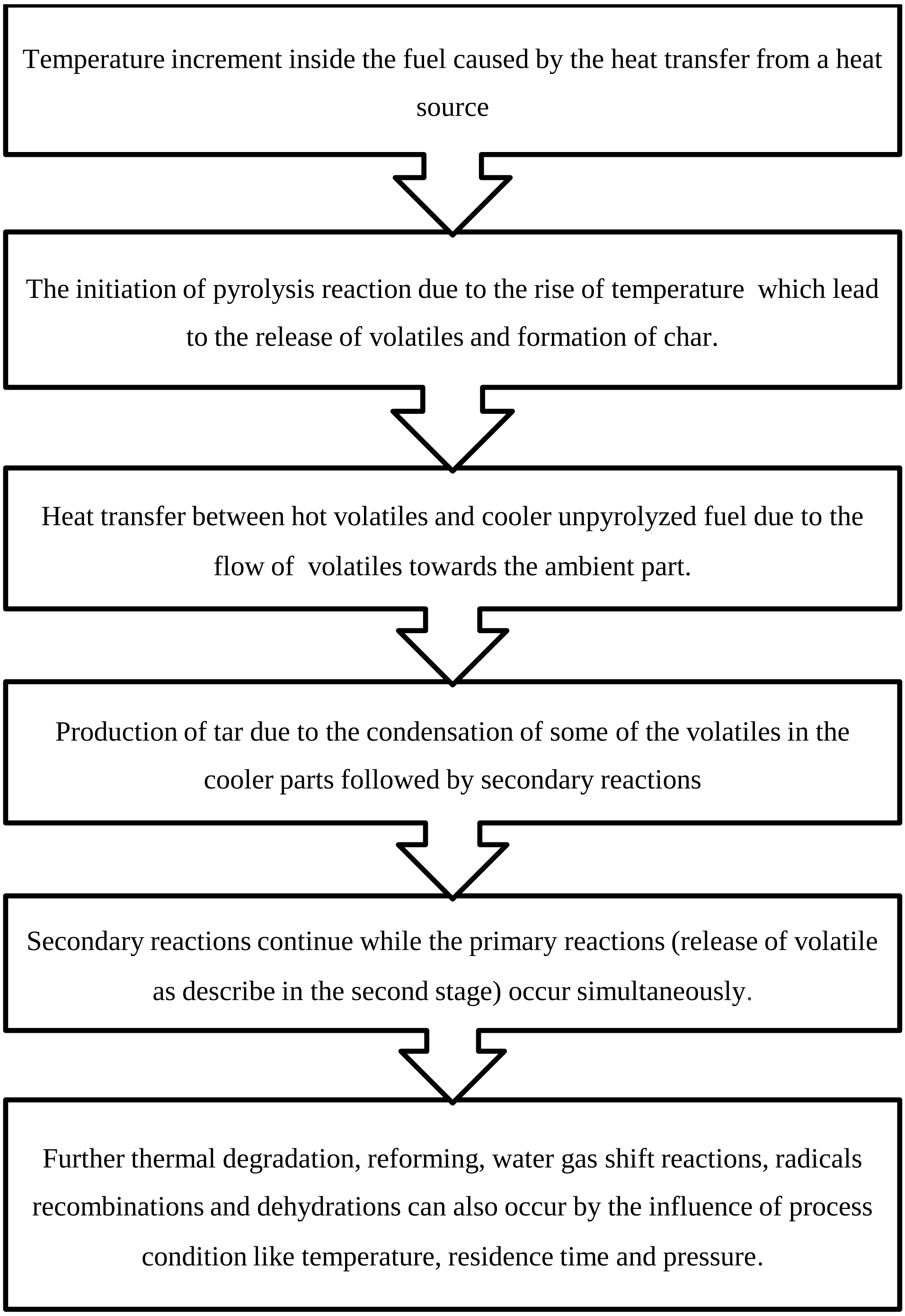

Figure 2.5: Flow of pyrolysis process

2.3.1 (a) Fast Pyrolysis

Fast pyrolysis is characterized by the high temperature and heating rate. It favors liquid or bio-oil and gas production. The biomass used for the feedstock of fast pyrolysis usually is finely ground due to the very high heating rate and heat transfer rate at the reaction interface (Bridgwater, 2003). Babu (2008) reported that fast pyrolysis involves the temperature ranging from 580 °C to 980 °C. Meanwhile Bridgwater and Bridge (1991) stated the temperature range for fast pyrolysis is around 450 °C to 900 °C.

Besides, the fast pyrolysis is capable of producing high yield of liquid up to 70 % wt on a dry feed basis in a lab-scale which involves the combination of high heating rate as high as 1000 °C/s to 10 000 °C/s, moderate temperature of less than 650 °C, and short residence time; 0.5 – 5 s (Bridgwater and Bridge, 1991). These conditions are the preferred parameters to maximize the production of pyrolysis oil. However, the terminal temperature can be increased at higher temperature if the production of gas is the major interest.

Various types of biomass feedstock such as residue from cassava plants (Pattiya, 2011), corn cobs and corn stover (Mullen et al., 2010), and oil palm wastes (Kim et al., 2010, Abdullah and Bridgwater, 2006) were used to study the influence of operation parameters and the production of bio-oil via fast pyrolysis process.

2.3.1 (b) Slow Pyrolysis

Slow pyrolysis is also known as conventional pyrolysis. This process favors char as the major product. It also produces liquid and gas. During the process, the feedstock will be heated at low heating rate and moderate temperature around 600 °C with the residence time varies from 5- 30 min (Basu, 2010, Bridgwater and Bridge, 1991). Compared to the fast pyrolysis process, the heating rate used in the slow pyrolysis process is quite low which is around 5 °C/min to 20 °C/min (Grierson et al., 2011).

Generally, the slow pyrolysis of dry lignocellulosic biomass could produce about 20 to 40 wt % of solid char or biochar (Lee et al., 2013). The percentages varied according to certain circumstances such as biomass properties, pyrolysis temperature, heating rate and residence time. From numerous studies conducted, temperature is recognized as the most influential parameter in the determination of the final product yield percentage and characteristics (Lua et al., 2004, Downie et al., 2009).

A significant amount of studies on slow pyrolysis have been carried out to investigate the impact of pyrolysis paramaters on the production and characterization of the biochar (Ghani et al., 2013, Gheorghe et al., 2009, Natarajan and Ganapathy Sundaram, 2009) and bio-oil (Duman et al., 2011) produced. Different types of biomass such as pine wood, wheat straw, green waste, dried algae (Ronsse et al., 2013), dry freshwater algae (Chaiwong et al., 2012), giant miscanthus (Lee et al., 2013), cherry seeds, cherry seeds shells (Duman et al., 2011), oil palm wastes (Khor, 2012, Khor and Lim, 2008), apricot stone, hazelnut shell, grapeseed and chestnut shell (Özçimen and Ersoy-Meriçboyu, 2010) were used as the feedstock in the slow pyrolysis process.

Lee et al. (2013) conducted a slow pyrolysis experiment on giant michantus to study the impact of pyrolysis temperature on the biochar yield and properties for soil applications using lab-scale packed bed reactor. The temperature were varied at 300 °C, 400 °C, 500 °C, 600 °C and 700 °C with heating rate of 10 °C/min. It was found that the percentage of biochar yield decreases from 49.54 wt % to 27.15 wt % as the temperature increased from 300 °C to 500 °C. However, after 500 °C, the decrement of biochar yield is quite insignificant. This is due to the decomposition of hemicelluloses and cellulose which has completed. Thus, the biochar production from giant michantus is appropriate at 500 °C by considering the properties of char and amount of heat required.

The decrement of char produced from the slow pyrolysis experiments as the temperature elevated were also observed in the other studies. In the study of slow pyrolysis of pomegranate seeds, the biochar yield decreases from 41.47 wt % to 27.87 wt % as the temperature increased from 400 °C to 800 °C (Uçar and Karagöz, 2009).

Duman et al. (2011) studied the slow pyrolysis of cherry seeds and cheery seeds shells in the fixed bed reactor at different pyrolysis temperatures. The temperatures were set at 300 °C, 400 °C, 500 °C and 600 °C. The feedstock was heated at 5 °C/min and 1 hour